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MOLECULAR COMPOSITES PROCESSING AND PROPERTIES I

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This report identifies a new approach to process thick molecular composites by non-melt consolidation. The process involves the coagulation of the PBT/Nylon 66 dope from methane sulfonic acid into a block of required dimensions using a specially designed mold. The coagulant diffused into the mold through a porous stainless steel plate while a constant pressure is applied to contain the volume changes during coagulation, thus giving a void-free coagulated block. Further consolidation was carried out in a press. The coagulation process was also accompanied by a study of the diffusion of coagulant into the dope. A power law relationship was established experimentally between the time required for coagulation and thickness of the dope. The experimental results were applied to the new coagulation process described above. Morphology study showed that if large voids are formed during coagulation, phase separated domains of 1-10 um size appeared on the void surface. Other scouting studies using steam as coagulant, multi-layer coatings and spraying dopes as droplets for fast coagulation were also reported.

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FOREWORD

This report was prepared by the Materials Laboratory, Nonmetallic Materials Division, and the University of Dayton Research Institute (UDRI) under Contract F33615-84-C-5020. This work was initiated under Project 241903, Work Unit Directive 24190310, "Advanced Composites" (WUD 45) in cooperation with Work Unit Directive 23030307 (WUD 43). Drs. S. Tsai and T. E. Helminiak were the AFWAL/ML Work Unit Directive Leaders of the respective Directives. Coauthors were: Drs. H. Chuah (UDRI), Charles Lee (MLBC), and T. E. Helminiak (MLBP).

This report covers research conducted from May 1985 to April 1986.

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SECTION 1
INTRODUCTION

Rigid rod aromatic heterocyclic polymers of PBX type are a new class of high-performance polymers synthesized by the Air Force Materials Laboratory. They showed high modulus of 40 to 50 mpsi and high strength of 400 to 500 kpsi. Based on specific modulus and strength, they out-perform metals, carbon fibers and Kevlar, thus offering the potential of replacing the state-of-the-art materials or new applications. The research in the application of these high-performance polymers is being actively pursued in the Air Force Ordered Polymer Program. Several new rigid rod polymers were synthesized. The three polymers which have been studied extensively are

Poly(p-phenylene benzobisthiazole) - (PBT)
Poly(p-phenylene benzobisoxazole) - (PBO)
Poly(p-phenylene benzobisimidazole) - (PBI)

An innovative idea in the application of these polymers is to homogeneously disperse the rigid rod molecules in a matrix of flexible coil polymer for reinforcement [1], analogous to a macroscopic chopped fiber composite but with the whole perspective of reinforcement taking place on a molecular level, thus resulting in a rigid rod molecular composite with enhanced mechanical properties.

PBX polymer degrades before it melts, therefore processing has to be carried out in a solution state with a strong acid such as methane sulfonic acid as the solvent. Not many flexible coil polymers can dissolve or are stable in the acid, thus limiting the choice of matrix polymers. Molecular composites based on PBT and a variety of flexible coil polymers: poly-2,5(6) benzimidazole (ABPBI) [2], PPQ [3], amorphous nylon and semi-crystalline nylons including Nylon 66 and its copolymers [4,5], and poly(ether ether ketone) (PEEK) [6], have been processed into either thin films or fibers. The resultant composites showed reinforcement of mechanical properties to various degrees. The

best reinforcement was achieved in the PBT/ABPBI system, with the modulus of a uniaxially oriented 30/70 molecular composite fiber at 17 mpsi [7], approaching that predicted from the Halpin-Tsai equation, thus validating the materials concept.

For structural applications, thick molecular composites are required. In an attempt to achieve this, the extruded thin films processed from solution were laminated by compression molding at elevated temperature and pressure. However, ABPBI does not melt and thus poses problems to this approach. Alternate flexible coil polymers such as nylons were used since they melt and can be molded at the nylon melting temperature such that the flow of nylon will bind the films together. However, this melt consolidation approach still failed to yield adequate adhesion between the film layers. It showed poor delamination strength under short beam shear failure [8].

The approach taken by the present task is a non-melt consolidation process by coagulating the dope of PBT/Nylon 66 directly into specimens of required thickness. The rationale is that the interfacial adhesive problem between films will be eliminated since the coagulated specimen is in one piece. This is a new approach and the task involved the following:

(1) The determination of the critical concentration, $C_{crit.}$, of the polymers in methane sulfonic acid. Below this concentration, the solution is homogeneous without the aggregation of rigid rod molecules prior to coagulation.

(2) Study of the diffusion rate of the coagulant into the dope such that a relationship between the dope thickness and coagulation time can be established.

(3) Investigate the dimensional changes, formability, morphology and mechanical properties after coagulation.

(4) Identify a viable method and study its feasibility for further development.

(5) Improve the identified coagulation method with a scale-up to obtain more samples for mechanical property investigations.

This was achieved through the use of a coagulation mold to be described in Section 3.

(6) Studies of other non-melt consolidation processes, such as lamination by spreading dope onto previously coagulated layers to build up the thicknesses. These miscellaneous methods are described in Section 4.

SECTION 2
DIFFUSION STUDIES IN PBT/NYLON 66 SOLUTION COAGULATION

INTRODUCTION

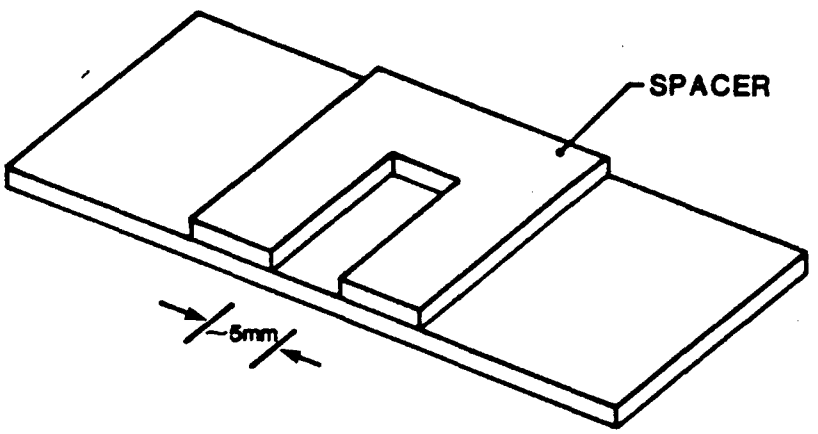
The approach taken in this task in processing molecular composites into thick specimens is to coagulate the PBT/Nylon 66 dope directly into a form of the required thickness. This approach is different from previous studies of thin film coagulation which occurs instantaneously when the dope came in contact with water and its subsequent lamination process. It is thus desirable to establish a relationship between the dope thickness and the coagulation time required. This study investigates the coagulation behavior of the PBT/Nylon 66/methane sulfonic acid (MSA) solution in water and the structural development during coagulation. The dimensional changes and the morphology of the coagulated dope are also studied. These studies are the primary steps in establishing the feasibility of direct coagulation.

EXPERIMENTAL

Diffusion Study

An optical mass transport method [9] was used to study the diffusion of coagulant into a PBT/Nylon/MSA dope during coagulation. PBT ($[\eta]$=21.4 and 24.7 dl/g) was obtained from Stanford Research International in the form of a dope in polyphosphoric acid. These dopes were coagulated and pulverized into PBT flakes as described in the Appendix. Nylon 66 is DuPont Zytel 42 with M_n=13,700. The dope was prepared by dissolving the polymers in MSA at 2 wt. % concentration, well below the critical concentration and stirred until the solution is homogeneous.

The optical mass transport method allows the diffusion process to be followed with an optical microscope as it occurs. The diffusion cell was made from a glass slide with spacers glued on top of it to provide a rectangular shape diffusion path of approximately 5 mm wide and 15 mm long (Figure 2.1). Spacers with



DIFFUSION CELL

Figure 2.1. Diffusion cell used in the optical mass transport method of measuring coagulation rate.

three thicknesses of 0.2, 0.4 and 0.6 mm were used to study any effect on the coagulation rate. The dope was placed in the cell path and sandwiched with a glass cover on top. We carefully ensured that the dope was contained within the cell path and did not flow over the spacer. Excess dope at the cell edge was wiped off. The diffusion cell was then placed in a petri dish on a specially constructed stage of an Olympus BH-2 optical microscope; the stage has a hydraulic actuator which moves the diffusion cell horizontally at a controlled speed such that the coagulation boundary is always in view in the microscope. The displacement was given by a digital readout of 0.001 mm. Due to the finite width of the cross-hair of the ocular, accuracy was estimated to be ±0.003 mm.

Distilled water as a coagulant was introduced at the diffusion cell edge. When coagulation occurs, the dope changes color from yellow-green to orange with the development of a distinct, sharp boundary. The movement of this boundary with time was followed by moving the diffusion cell with the actuator so that the boundary was in line with the cross-hair of the microscope ocular. The distance of the boundary from the cell edge was recorded. All diffusion studies were done at room temperature.

In this setup, structural development in the dope during coagulation was also photographically recorded.

Study in Dimensional Changes

Dimensional changes of the dope during coagulation were studied by spreading it on a glass plate into squares of 2 and 4 cm respectively and with thickness ranging from 0.5 to 5 mm thick.

The dope was coagulated in water without any constraint imposed on it. The dimensions before and after coagulation were measured. Bulk density of the coagulated dope was measured by a flotation method [10], by suspending it with a thin wire in a

balance to measure the weight in air and when immersed in distilled water. Volume of the coagulated dope was computed from the bulk density.

The coagulated dope was further consolidated by pressing it between layers of filter paper, with slowly increasing pressure up to 3,000 psi in a Carver hand press. The water squeezed out during pressing was blotted out by the filter papers which were changed frequently. Further drying was continued in a vacuum oven at 100°C for 48 hours. The density after consolidation was measured by the flotation method as described above.

Morphology of Coagulated Dope

The bulk coagulated dope was dried in air and fractured in liquid nitrogen for morphological studies. The fracture surface was coated with gold and was examined in an Alpha-9 scanning electron microscope (SEM). For X-ray microanalysis, carbon coated sample was used in an ETEC scanning electron microscope. However, discharge is often encountered in the carbon coated samples. To overcome this, the sample was first coated with gold and then freeze fractured; the new surface was coated with carbon such that the gold coated sides conduct to prevent discharge. In this way, X-ray microanalysis could be done on the observed large domains of 10 μm.

RESULTS AND DISCUSSION

Diffusion Study

The objective of this task is to explore the feasibility of directly coagulating a PBT/Nylon 66 dope into a bulk molecular composite of required thickness. Previous studies [4,5] established the materials concept of molecular composite based on a PBT and Nylon 66 system by extruding its solution into thin film in which coagulation takes place instantaneously such that the structure of the homogeneously dispersed polymers is largely preserved. For coagulation of the dope into a bulk form, the diffusion of coagulant into the dope plays a major role in determining the processing time and the accompanied structural development, yet no data are available except the diffusion

studies in the spinning of PBT dopes [11]. This study investigates the coagulation of PBT/Nylon 66/MSA dopes in water to provide information as to how long it takes to coagulate a dope in bulk with the required thickness. The method of diffusion study is based on that of Berry et al. [11] who investigated the coagulation of PBT dope with various solvents as coagulants, using an optical method. A modification is made by using a diffusion cell described in Hakemi and Krigbaum's [9] optical mass transport method. In this method, diffusion is followed by an optical microscope as it occurs. The cell is set up such that diffusion of the coagulant into the dope starts from the cell edge and travels inwards into the cell path. If we envisage that the cross section of the cell perpendicular to the direction in which coagulation takes place as the surface of a bulk dope, diffusion along the cell path is then equivalent to the thickness direction of the bulk dope. Thus, this setup enables the study of a relationship between the thickness of a bulk dope and coagulation time.

When coagulation occurs, the dope changes color from yellow-green to orange. A boundary between the coagulated phase and the solution phase is formed at a distance x from the cell edge and moves as coagulation proceeds. This distance is followed with respect to time t by moving the actuator of the microscope stage. The plots of log x vs log t for dopes with 30/70, 70/30 and 100/0 PBT/Nylon 66 contents are shown in Figure 2.2. They showed good linear correlation, with $r>0.99$. From these linear plots we concluded that coagulation of the PBT/Nylon 66 dopes at room temperature follows a power law relationship

$$x = kt^n \qquad (2.1)$$

where k is a constant and n is the power law index obtained from the slopes of log x vs. log t plots.

Since the high viscosity dope was contained in the diffusion cell in contact with glass slides and separated by a thin spacer

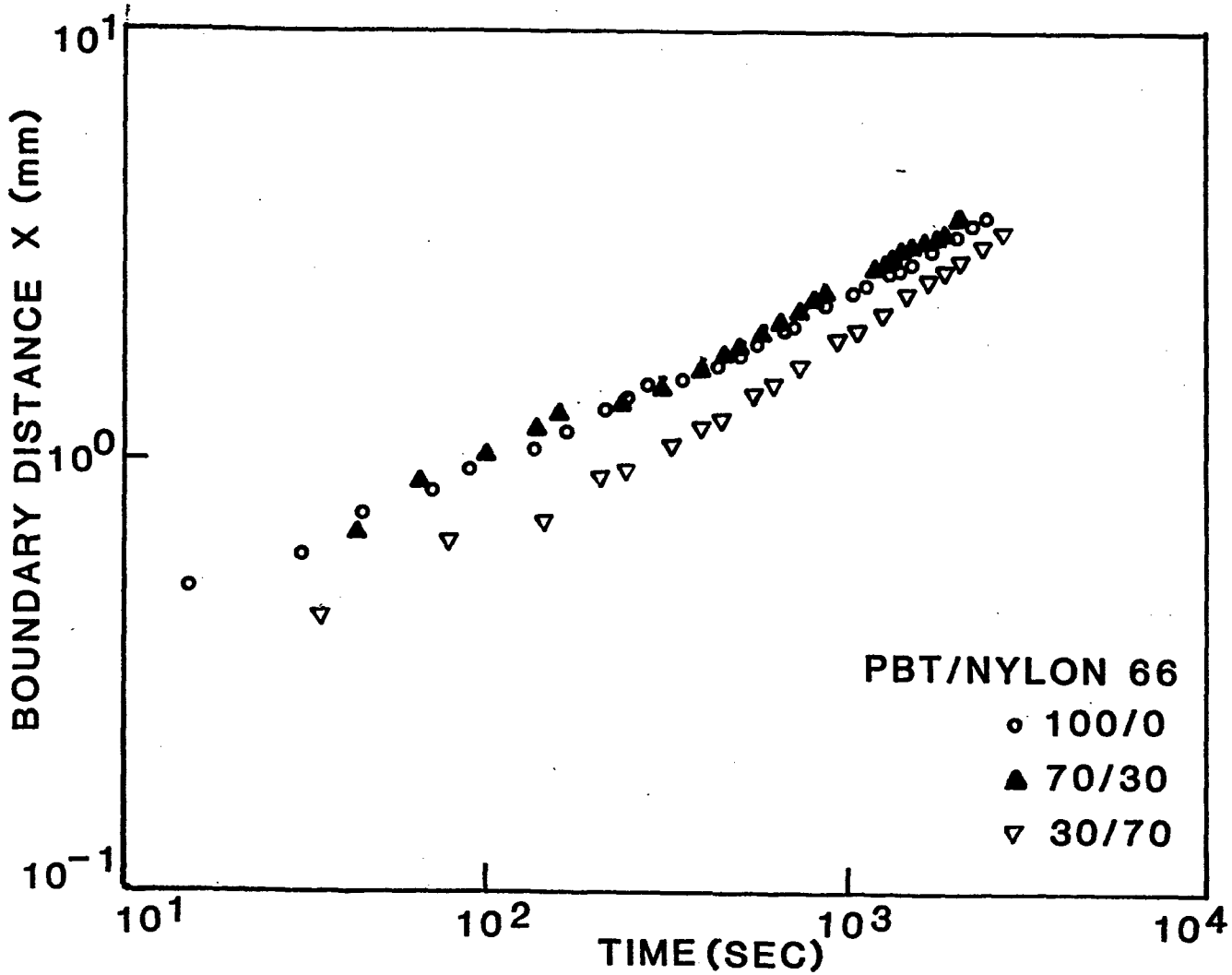


Figure 2.2. Plot of boundary distance vs. coagulation time for 100/0, 70/30 and 30/70 PBT/Nylon 66/MSA 2.0 wt. % dopes.

0.2 mm thick. We speculated that the stress induced at the contact surfaces between the dope and the glass slides could affect the measured coagulation rate and behavior. Tests were carried out by putting the diffusion cell filled with the dope in a desiccator for 72 hours for slow annealing to relieve any possible induced stress. Diffusion study of such annealed dope did not show significant changes in the coagulation behavior. Another test was to increase the spacer thickness such that the cross-sectional area of the cell path is increased. Should there be changes in the coagulation rate, the one resulting from thicker spacers and therefore larger cross section in which coagulation takes place would approximate closer to that of the bulk dope. Spacers 0.4 and 0.6 mm thick were used. We found that when the thickness exceeds 0.6 mm, shrinkage of the dope during coagulation caused the coagulated phase to pull away from the glass surface of the diffusion cell allowing water to seep in between the dope and glass. Diffusion in this case is therefore not uniform across the cross section of the cell path and appeared to be much faster. The power law indices obtained with different spacer thicknesses are shown in Table 2.1.

We found that changing the spacer thickness did not change the power law index, n, significantly. For dopes with different PBT/Nylon 66 contents, the plots of log x vs. log t (Figure 2.2) were shifted vertically upwards as the PBT content was increased. Thus the intercept which gives the constant k of the power law equation is therefore higher for dope with higher rod content.

The index n is not significantly affected by the compositions of PBT and Nylon 66 studied, and varies from 0.40 to 0.46 in the series. From the experimental values of k and n, the time required to coagulate bulk dope of thickness x can be predicted. On doubling the dope thickness, it was estimated that the coagulation time has to be increased by five to six times. Therefore bulk coagulation into thick specimens is a slow process.

During coagulation, a distinct boundary is formed separating the gel-like coagulated phase from the uncoagulated dope and it

TABLE 2.1

POWER LAW INDEX, n AND COAGULATION RATE OF PBT/NYLON 66 DOPE COAGULATED WITH WATER AT ROOM TEMPERATURE

	Spacer Thickness (mm)	PBT/Nylon 66 Composition 30/70	70/30	100/0
n	0.2	0.46	0.42	0.40
	0.4	0.40	0.41	-
	0.6	0.44	0.43	-
Coagulation Rate ($mm/s^{1/2}$)	0.2	0.059	0.071	0.067
	0.4	0.057	0.059	-
	0.6	0.063	0.073	-

moves as coagulation proceeds. Such behavior can be described by a moving boundary diffusion model. Several models [12] have been proposed to provide theoretical background of some important processes, such as a chemical reaction between two phases as in the corrosion of metals [13], phase transition or the coagulation of fiber during spinning process in which solidification occurs with the growth of a coagulated skin layer [14].

These theoretical models were largely developed by Hermans [15], Fujita [16], Takizawa [17], Griffin and Coughanover [18]. Jost [19] generalized the solutions to the moving boundary models into five cases which involve different boundary conditions and further provided cases in which the boundary consists of a diffuse, intermediate region. A model based on that of Jost is set up to describe the coagulation of PBT/Nylon 66 dope by water in this study.

If we consider the uncoagulated dope as a single phase with a ternary system of PBT, Nylon 66 and MSA as shown in Figure 2.3, when a coagulant is added, it exchanges with MSA through diffusion thereby coagulating the dope into a gel-like phase 2. If the boundary formed at x' is sharp, which is the case in the initial stage of coagulation before the observation of a narrow intermediate band ahead of the boundary, and that the coagulant does not spill beyond the boundary into the uncoagulated dope, diffusion can be described by Fick's law:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \qquad (2.2)$$

assuming that the diffusion coefficient, D, is independent of concentration, c.

The boundary conditions are:

$$c=0, \quad x=0, \quad t=0 \qquad (2.3)$$

$$c=c_o, \quad x=0, \quad t>0 \qquad (2.4)$$

$$c=c_b, \quad x=x'_{-0} \qquad (2.5)$$

$$c=c, \quad x=x'_{+0} \qquad (2.6)$$

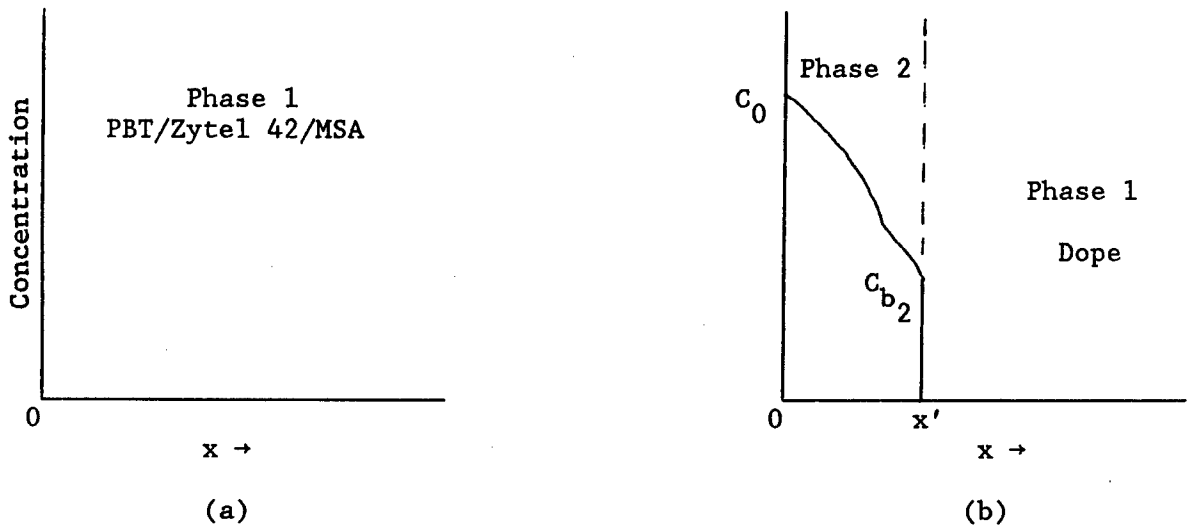


Figure 2.3. Moving boundary model for diffusion before and after formation of a second phase.

At the boundary, mass balance of an infinitely small dx and dt gives:

$$c_{b_2} dx = -D(\frac{\partial c}{\partial x})dt \qquad (2.7)$$

Solutions to the differential equations are

$$c = c_o - B \text{ erf } (\frac{x}{2\sqrt{Dt}}) \qquad (2.8)$$

and

$$x = \gamma 2\sqrt{Dt} \qquad (2.9)$$

Substituting the differentials of the above into equation 2.8 gives the constant, B.

$$B = c_{b_2} \gamma\sqrt{\pi} \exp \gamma^2 \qquad (2.10)$$

The solution can be further simplified into the form

$$\frac{c}{c_o} = \frac{1}{1 + \gamma\sqrt{\pi} \exp \gamma^2 \text{ erf}\gamma} \qquad (2.11)$$

describing the concentration profile of the coagulant in phase 2. At x=0, c/c_o=1 and diminishes with increasing distance x. D can be found only if c/c_o is known. However, determination of the profile is difficult at this stage. More important is that the solution of equation 2.9 shows that the boundary distance x is a function of t to the power of 0.5, which is in close agreement to the power law index obtained from the experiment. Therefore, the coagulation process can be approximated as a Fickian diffusion.

From the optical microscope observations, the boundary at the later stage of coagulation showed the development of a faint, but distinct second boundary, forming a narrow band instead of a sharp boundary (Figure 2.4). This intermediate band is much clearer when observed under crossed-polars and did not appear to alter the power law relationship. The band formed is 0.1 mm wide

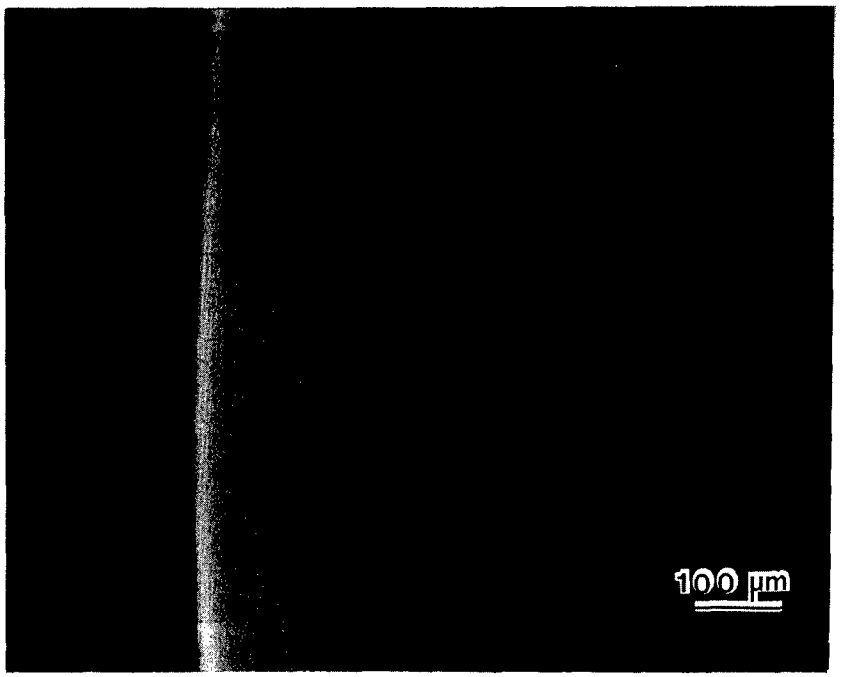


Figure 2.4. Formation of intermediate band at the boundary.

and is perhaps a region where there is an exchange of MSA and water without the full gelation of the dope. Therefore, a closer model for this case will be the one shown in Figure 2.5. In such a model, the solutions to Fick's law will be

$$\frac{c_{b_2} - c_{b_1}}{c_{b_1}} = \sqrt{\pi}\,\gamma''\exp(\gamma''^2)[\mathrm{erf}(\gamma'') + \mathrm{erf}(\gamma')]$$

$$\frac{c_{b_2} - c_{b_1}}{c_o - c_{b_2}} = \sqrt{\pi}\,\gamma'\exp(\gamma'^2)[\mathrm{erf}(\gamma'') + \mathrm{erf}(\gamma')] \qquad (2.12)$$

The diffusion constant cannot be measured without knowing the concentration profile, and the experimental power law index n approaches 0.5 as predicted by a moving boundary diffusion model. A convenient way of comparing the coagulation behavior is to plot x vs $t^{1/2}$ according to equation 2.9, which gives a slope of $2\gamma\sqrt{D}$, incorporating the diffusion constant. Berry [11] used this slope as the coagulation rate.

The data of Figure 2.2 were replotted in this form and gave good linear correlation with intercept at the origin (Figure 2.6). The coagulation rates obtained from the slopes are shown in Table 2.1. We found that the rate was not significantly affected by the spacer thickness within experimental errors. It increases slightly with higher PBT content, 0.059 mm/sec for a 30/70 dope to 0.071 for a dope with 100% PBT which agrees well with the result reported by Berry [11]. The results showed that PBT content has only small effect on the coagulation rate. Significant changes in the rate can only be brought about by changing the nature of the coagulant and temperature.

An alternate form of expressing the coagulation rate which is used in the study of fiber coagulation during spinning [14] is to plot the data in the form of x^2 vs t. The rate is expressed as the growth rate parameter G:

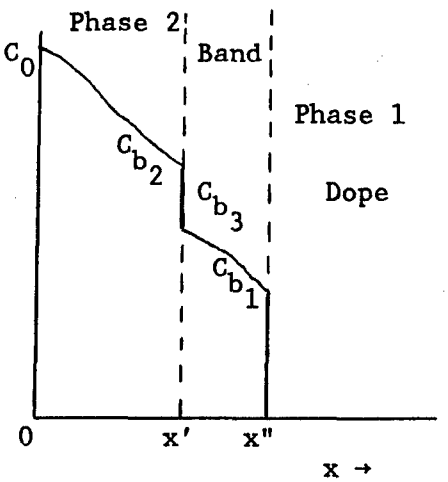


Figure 2.5. Moving boundary model with an intermediate band.

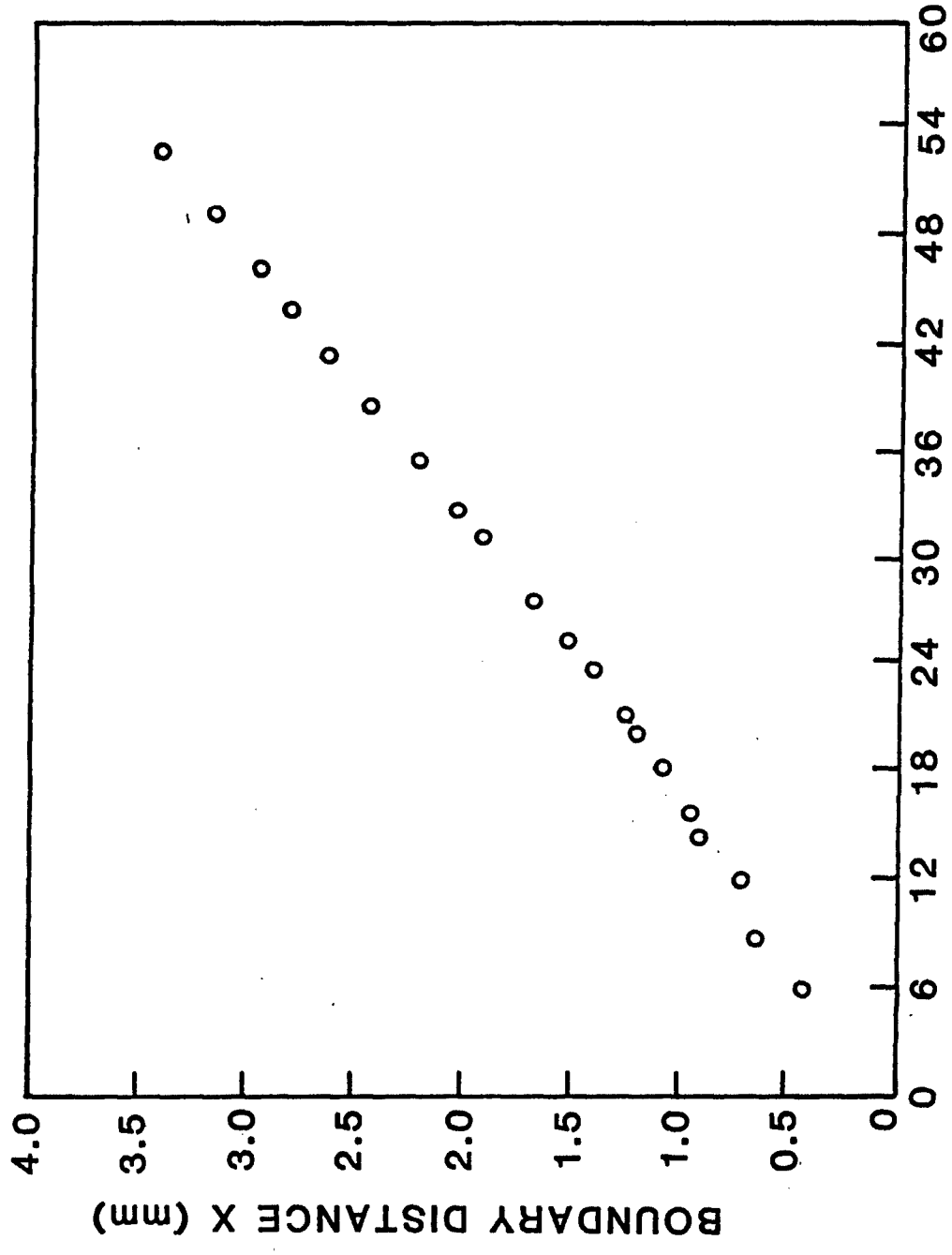


Figure 2.6. Plot of boundary distance vs. square root of time.

$$G = \frac{1}{4} \lim_{t \to 0} \left(\frac{dx^2}{dt}\right) \qquad (2.13)$$

which reflects the effects of spinning dope and bath compositions, temperature, etc. G in this case depends only on the rate of mass transfer between the phases.

When the dope was coagulated, close examination with an optical microscope showed structural development in the coagulated gel-like phase. Such structural formation varied at the different stages of coagulation. Initially, a narrow homogeneous, orange-red zone was formed near the cell edge where the coagulant was introduced, and followed by the development of numerous, very fine finger-like structure. The homogeneous region occurs for all the dopes studied, however, the width is variable and ranges from 0.02 to 0.3 mm wide. It is likely that this homogeneous phase at the onset of coagulation is similar to the skin in a skin-core formation observed in fiber spinning, except that the thickness observed here is much larger. Subsequent coagulation of the bulk dope without any constraints imposed on the dope showed the formation of a skin-like surface surrounding the bulk coagulated dope.

The formation of the finger-like structure initiates with numerous, but small, branches ahead of the homogeneous region and proceeds toward the moving boundary as coagulation occurs (Figure 2.7). At the same time, they become broader and coalesce with adjacent ones to form bigger branches (Figure 2.8). At some point, they become so wide that a homogeneous phase is reformed. This occurs in the 70/30 system for all the different thickness spacers and in the 30/70 system with 0.6 mm thick spacers.

When the dope is coagulated, especially with thicker spacers, incursions are observed. This occurs about 1 to 5 minutes after coagulation and gave the appearance that the coagulant is ahead of the boundary forming a well-defined lobe (Figure 2.9). As coagulation proceeds, numerous incursion lobes are formed and they impinge on each other sideways and join together. We also observed that the incursion lobes are formed

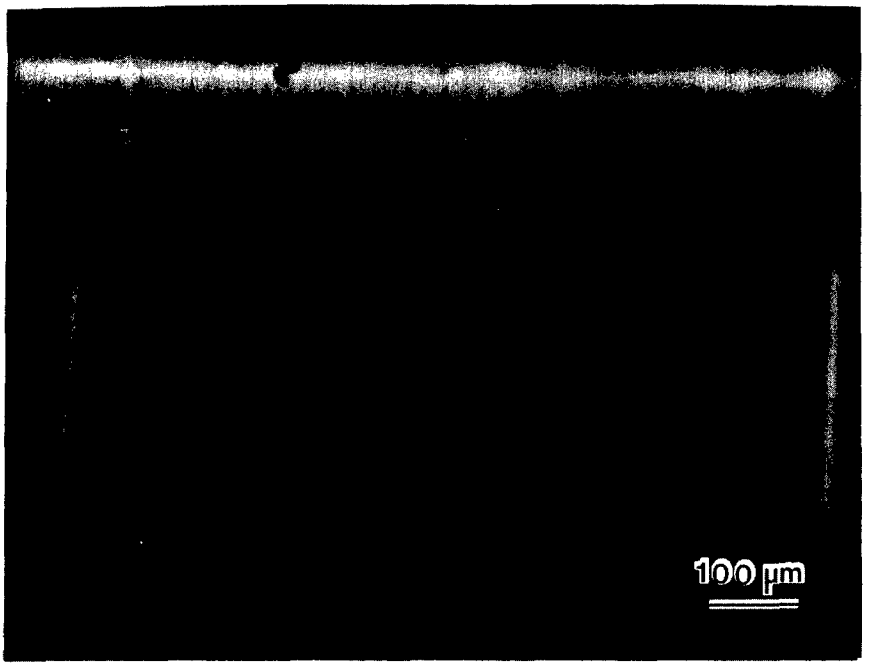


Figure 2.7. Development of finger-like morphology during coagulation.

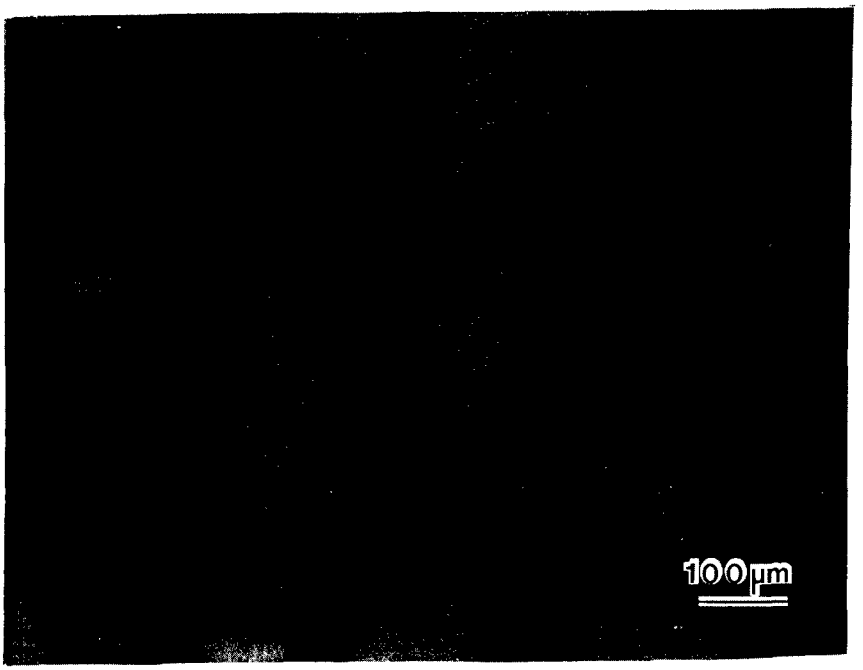


Figure 2.8. Development of finger-like morphology during coagulation.

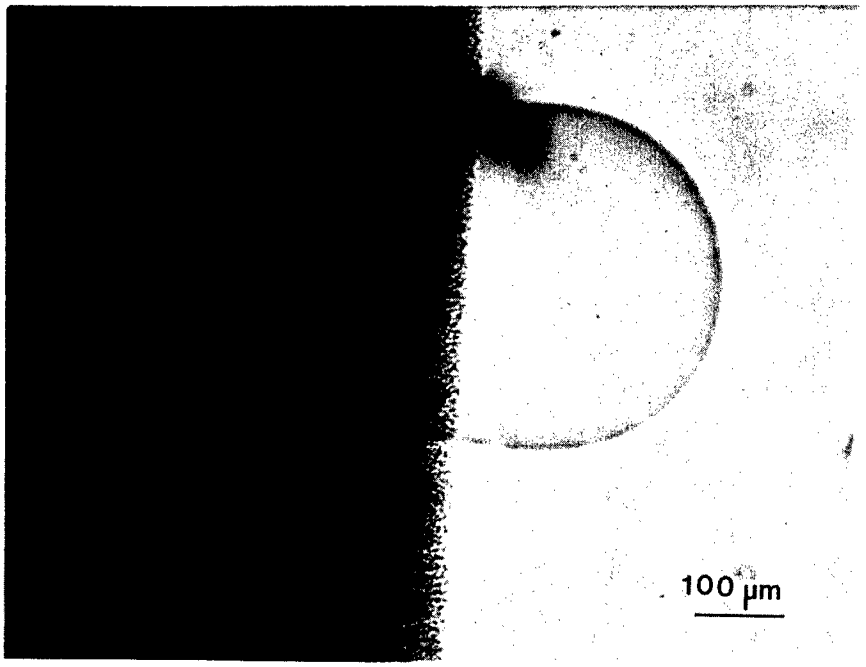


Figure 2.9. Incursion lobe formation at the boundary.

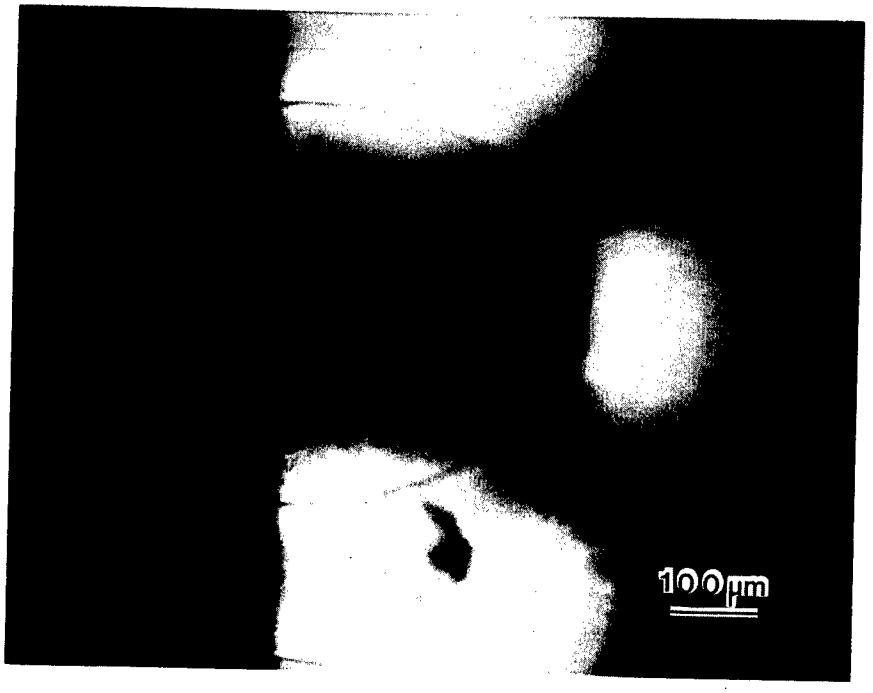


Figure 2.10. Incursion lobe under cross-polars.

between the branches of the finger-like structure. Under crossed polars, the lobe extincts with its surrounding slightly birefringent (Figure 2.10). The occurrence of the lobe must have induced local orientation in the dope surrounding it.

From these observations, it is likely that incursion is due to the surface effect between the coagulated dope and the glass slide. Due to shrinkage, the volume contraction of the coagulated dope causes it to separate from the glass slide at a certain point, forming an air gap which propagates towards the boundary. We also noticed that after coagulation, the surface of the coagulated dope showed some depressed streaks on its surface, pointing to the evidence of air gap formation. Therefore, incursion lobes observed here could be an artifact and possibly do not appear in bulk coagulation.

Dimensional Changes During Coagulation

When the dope is coagulated without any restraint imposed on it, its dimension changes. Such changes are to be expected, since there is an exchange of mass between MSA and water which have different densities. The dimensional changes appeared to be dependent on the initial dope thickness. It is thus desirable to find out how the initial thickness of the dope affects the final coagulated dimensions since the objective of the present task is to bulk coagulate thick molecular composites.

A 70/30 PBT/Nylon 66 dope was spread on glass plates to form squares of 2x2 and 4x4 cm, and with different initial thicknesses. On coagulation, the dope with initial thickness <1 mm showed little changes in both the lateral and thickness dimensions. However, when the initial dope thickness is >1 mm, there is a drastic change in thickness as well as the overall shape of the coagulated dope. The dope bulges out in the center and tapered gradually towards the edges, accompanied by shrinkage in the lateral dimensions, into a final shape of a charcoal briquet as in Figure 2.11. It also appeared to form a tight skin surface. Since the thickness changes are not uniform, the thickest dimension in the center was measured.

Figure 2.11. Shape changes after bulk coagulation without any restraint imposed on the dope.

The % increase (Figure 2.12) in thickness is a function of the initial dope thickness. There is very little difference in the dimensional changes for dope either 2x2 or 4x4 cm square when the initial dope thickness is <1 mm. The % thickness increase is 10% and is followed by a sudden increase when thickness is >1 mm up to 360% at thickness = 2 mm after which the % increase drops to ~200%. Comparing the small increase in thickness when the initial dope thickness is <1 mm to the observation of a homogeneous region when the coagulant was first introduced in the diffusion study, it is likely that a homogeneous skin was formed. While there is an apparent large increase in thickness, the lateral dimensions decrease and remain nearly constant at ~50% irrespective of the initial dope thickness (Figure 2.13).

The bulk density of the coagulated dope determined by the flotation method is shown in Figure 2.14. It decreases with increasing dope thickness. When the coagulated dope was sliced open, it had a large number of voids. The voids are smaller near the outer edges and increase in size to the order of mm at the center of the coagulated dope and are interconnected. Apparently the increase in initial dope thickness forms more and larger voids. Such void formation is likely to be associated to the development of finger-like structure from fast coagulation.

The presence of large voids and capillaries are also found in wet-spun fibers but not in dry-spun fibers of polyvinyl alcohol pointing to the evidence that they are caused by the coagulation process [14]. The mechanism of their formation has been attributed to the formation of a heterophase system with small pores filled with both the solvent and nonsolvent [20]. Mass transport within the pores is faster than the diffusion through the bulk of the coagulated mass and results in the rapid growth of these pores into large voids. Other explanations include the cracking or the tearing effect of the coagulated mass as a result of volume shrinkage. The void formation can be suppressed by using a lower power coagulant or lowering the

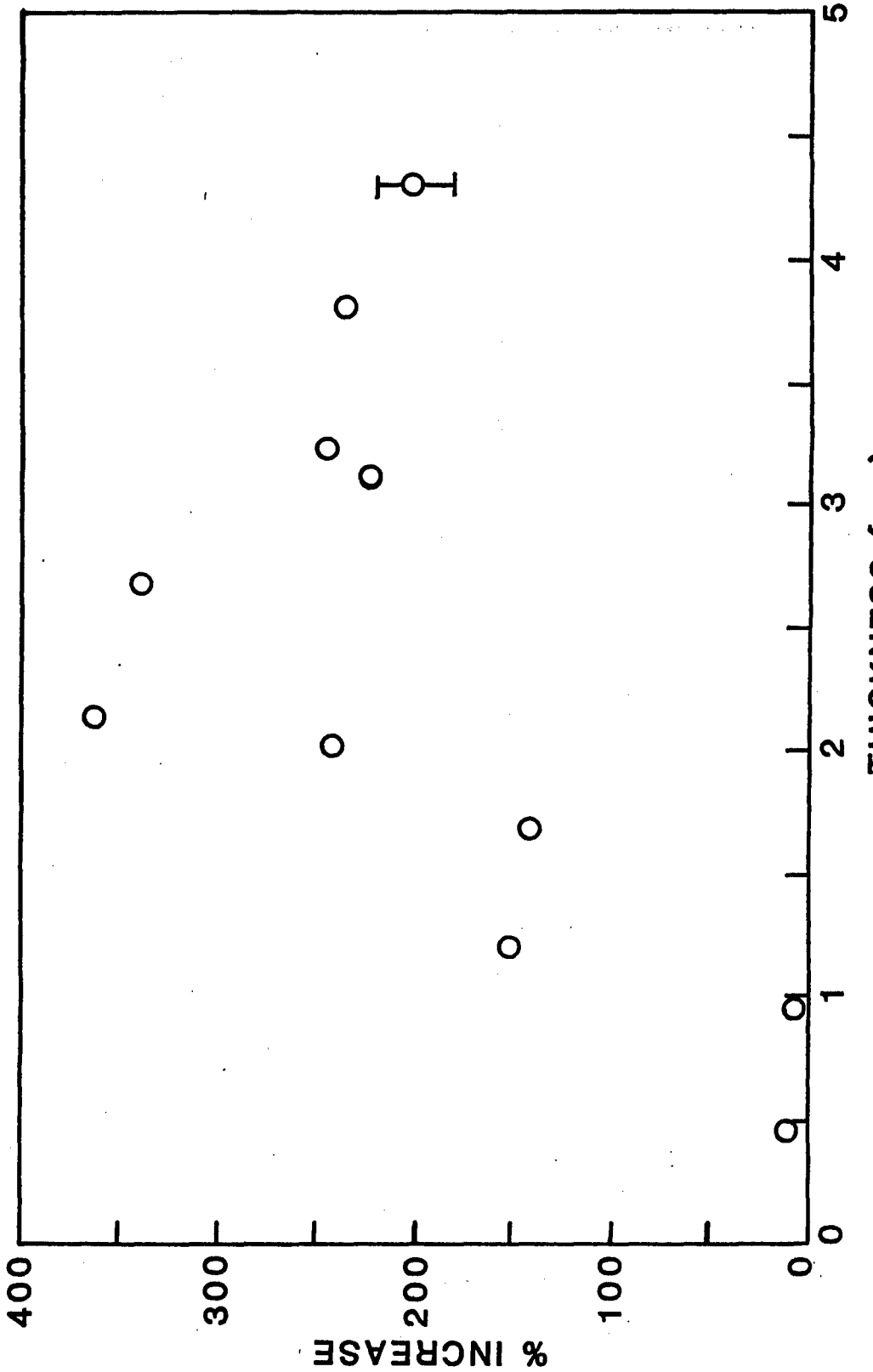


Figure 2.12. % Increase in thickness as a function of initial dope thickness.

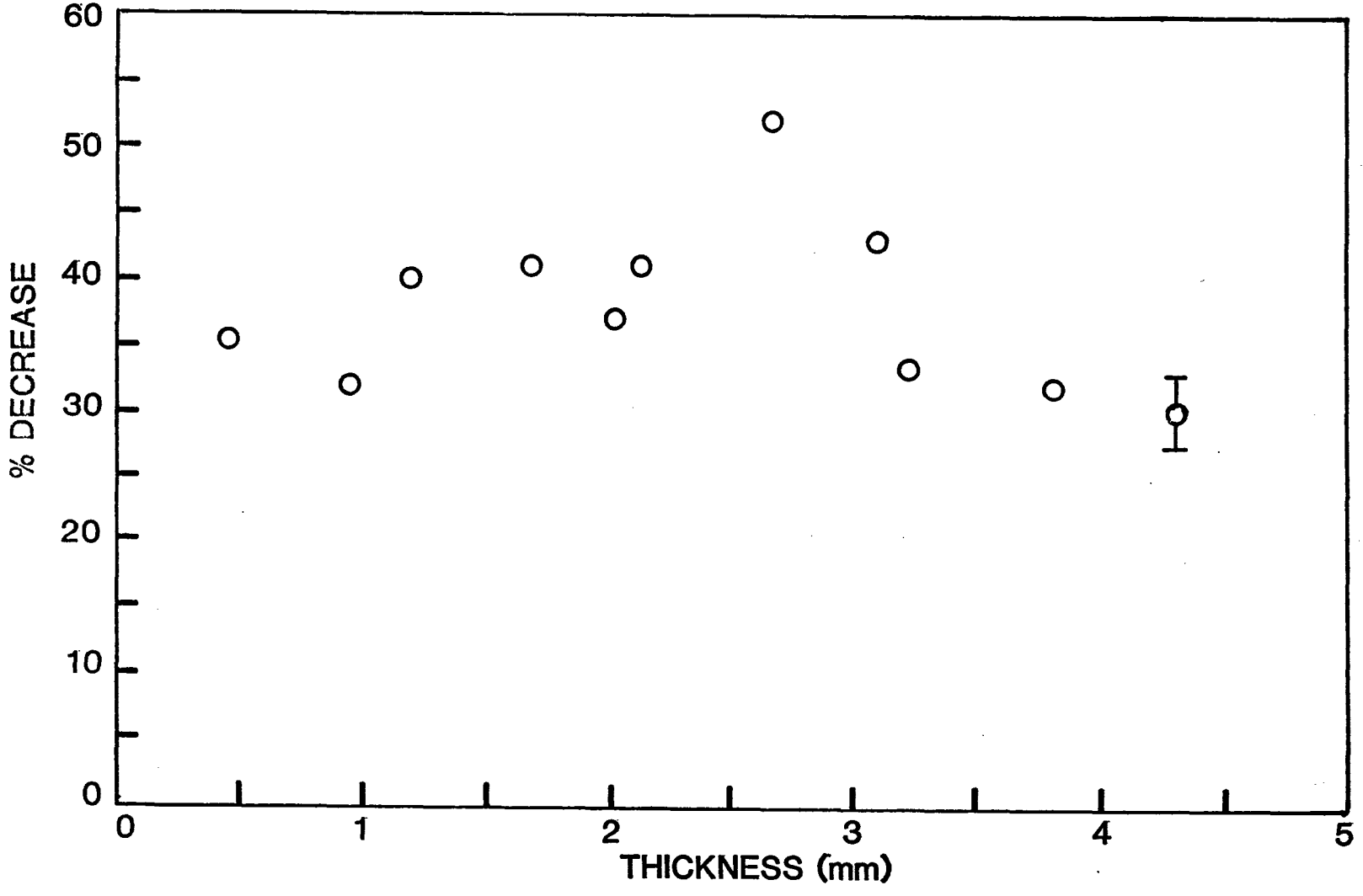


Figure 2.13. % Decrease in lateral width as a function of initial dope thickness.

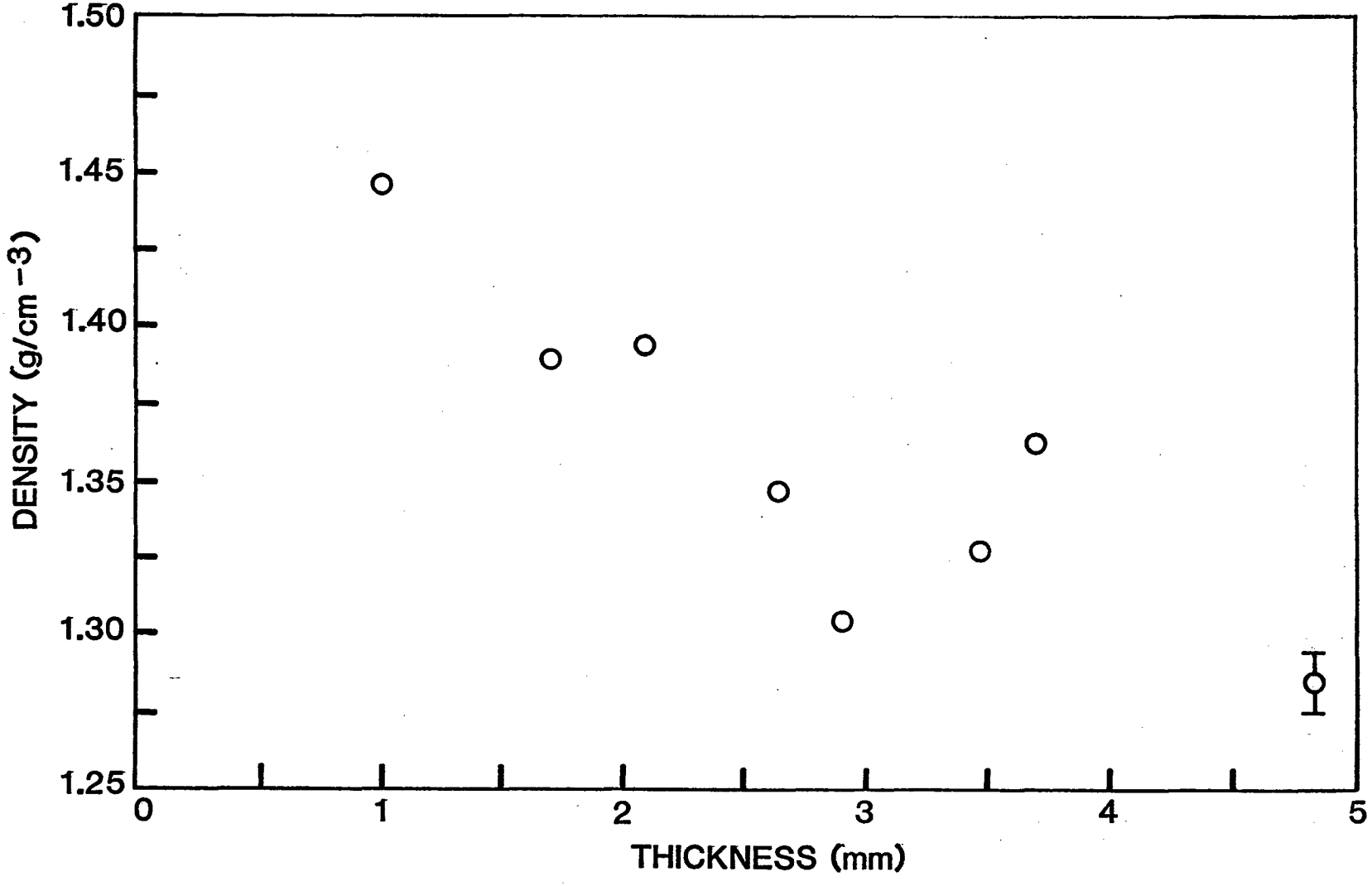


Figure 2.14. Density of a consolidated 70/30 dope as a function of initial dope thickness.

coagulation bath temperature [14], thus pointing to the importance of phase equilibria between the solvent, nonsolvent and polymers during coagulation.

Because of the increasing amount of voids as the dope thickness is increased, the bulk density of the coagulated dope decreases. However, it is not possible to estimate the void content from the density and weight measurements since the coagulated dope is still wet, containing an undetermined amount of water and remaining MSA. However, the volume can be calculated from the apparent density which shows an approximately 50 to 60% decrease when the dope thickness is >1 mm and becomes less as the initial thickness is increased. The apparent smaller decrease in volume with increasing dope thickness is an artifact since it is accompanied by the corresponding increase in undetermined larger voids which make a substantial portion of the volume (Figure 2.15). Taking this into consideration, it is likely that the % volume shrinkage stays at a constant level of 50 to 60%.

The dopes were consolidated, after washing to remove MSA, by squeezing out water in a press and further dried in a vacuum oven. On comparing the final volume to that calculated from the rule of mixture based on PBT and Nylon 66 contents and densities (densities of PBT and Nylon 66 are 1.60 and 1.14 g/cm^3 respectively), we found that the final volume after consolidation is much higher than expected and could only be due to the voids which could not be eliminated completely during consolidation. Final void content is ~0.3% when the initial dope thickness is <1 mm and increases to 10% with thicker initial dope as a result of having more and larger voids (Figure 2.16). The low void content and the observed small % increase in thickness upon coagulating dope with initial thickness of <1 mm indicates that even with water as a fast coagulant, void formation is not a significant problem when it is below this critical thickness for coagulation. With increasing dope thickness, void formation becomes a major problem accompanied by the formation of phase separated domains on its surfaces, discussed below.

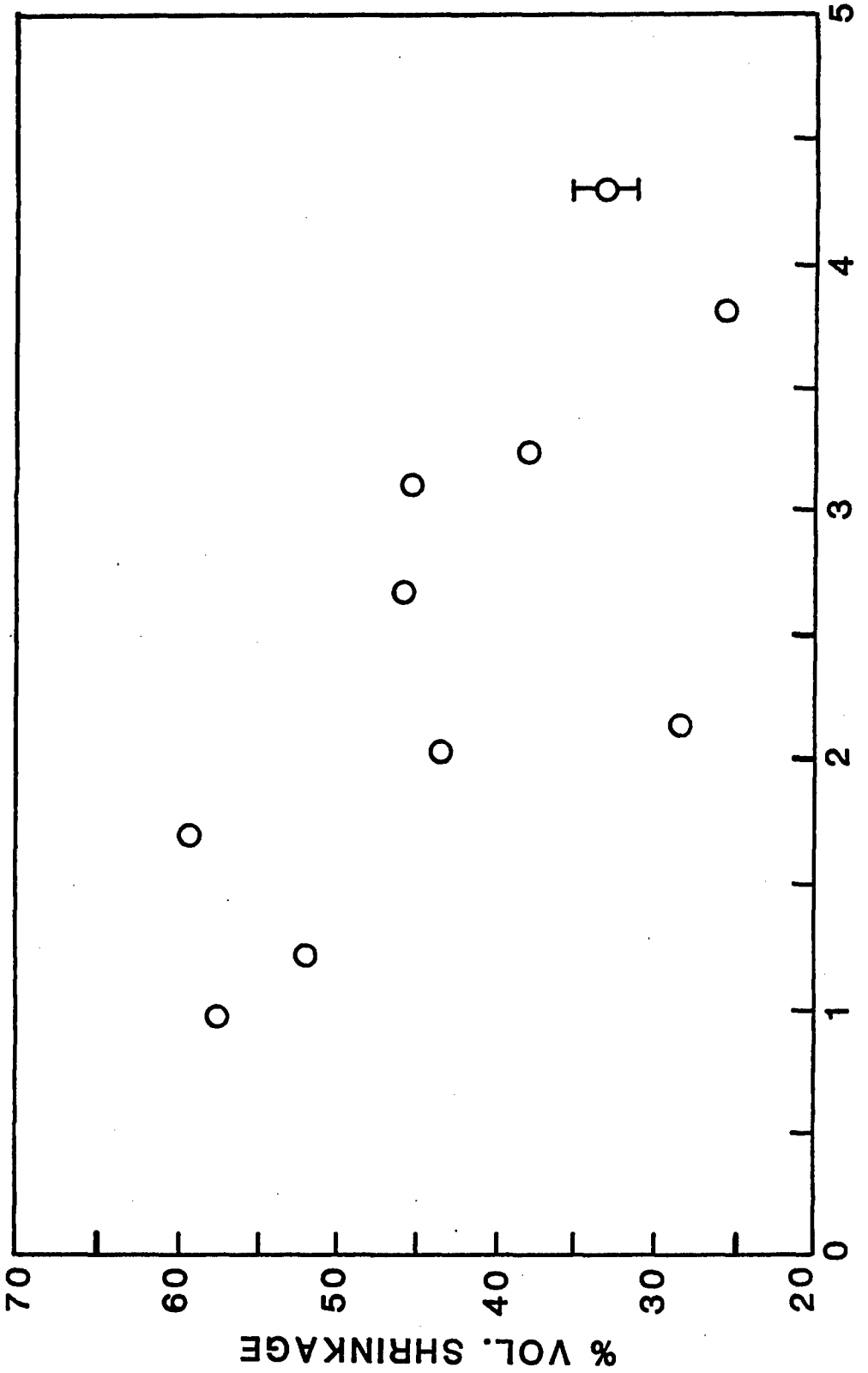


Figure 2.15. % Volume shrinkage as a function of initial dope thickness.

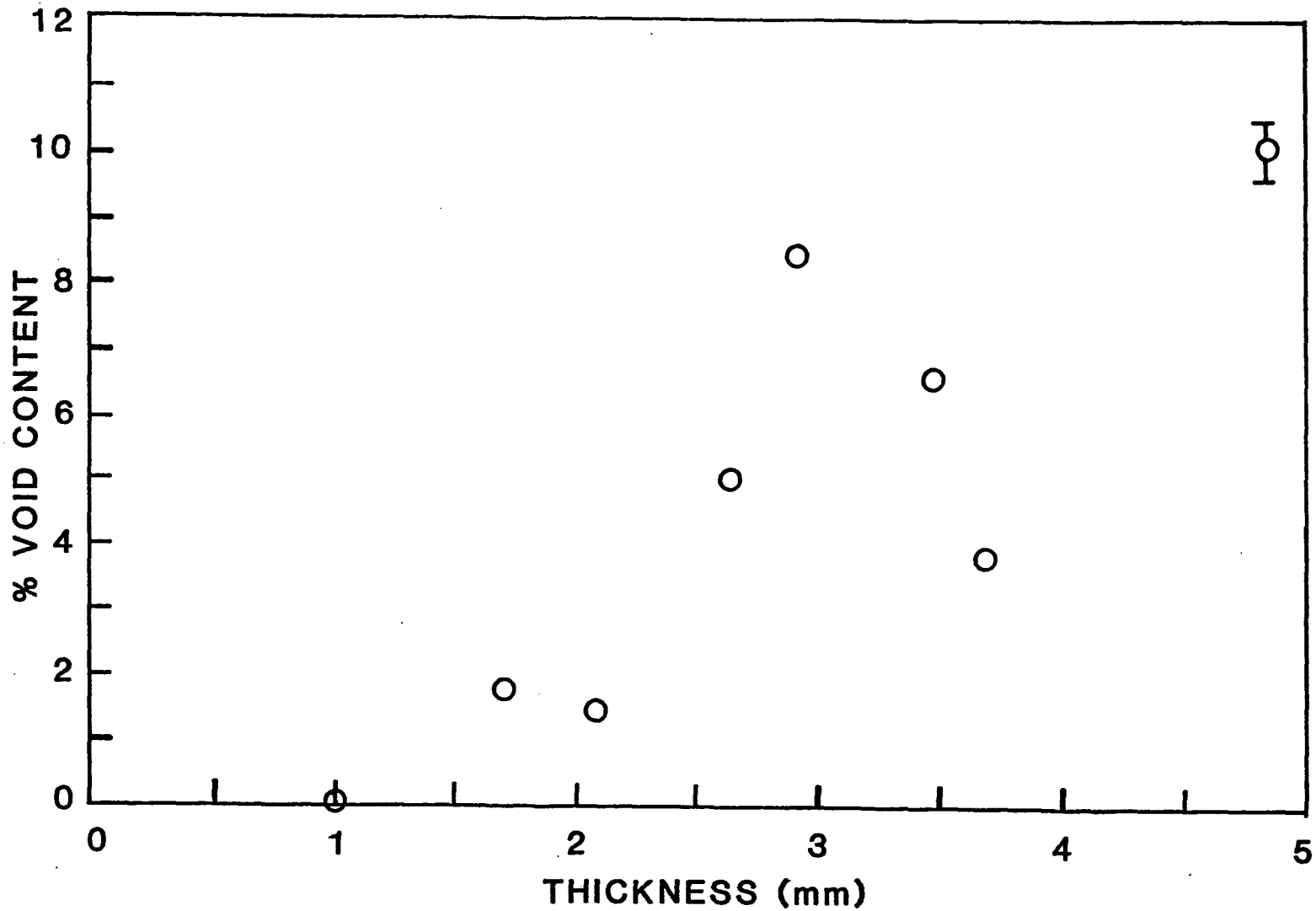


Figure 2.16. % Void Content after consolidation as a function of initial dope thickness.

Morphology

In molecular composites, one of the most important questions on the morphology is whether the rigid rods are homogeneously dispersed in the flexible coil host matrix. Thermodynamically, the rod/coil system in a solution state is only compatible at below a critical concentration, C_{crit}, which was determined to be ~3-6% depending on the PBT/coil composition [21]. Such C_{crit} decreases as the rod content is increased. When coagulation takes place, MSA is exchanged with a nonsolvent such that the concentration of the dope increases. To prevent gross phase separation, kinetically, coagulation must be fast enough such that the homogeneous nature of the system in solution is frozen, overcoming the unfavorable thermodynamic driving force for phase separation. In the extrusion coagulation of thin film ~3 mil thick, the immediate coagulation on contact with water produced optically clear film. Dark-field TEM work on a 55/45 PBT/Nylon 66 film did not show Nylon aggregates larger than 50-100 A [22]. However, when a PBT/ABPBI film was cast by evaporating the solvent through evacuation, the slow change in concentration to above C_{crit} produced extensive phase separation with the formation of ellipsoidal domains of 2 to 3 μm long as observed in the fracture surface in SEM. Such type of phase separated domains have been called "football" morphology, and was largely made up of PBT [23].

Bulk coagulation of the dope without any physical restraints caused tremendous changes in dimensions and formed numerously large voids. In terms of morphological investigations, two regions are of interest: the surface of the voids and the fracture surface of the bulk.

A 70/30 PBT/Nylon 66 coagulated dope was air dried and freeze fractured in liquid N_2. Studies of the fracture sample by SEM reveal large voids on the order of 100 μm (Figure 2.17). The surfaces of the voids were rough with overgrowth. The area surrounding the voids (Figures 2.18 and 2.19) is the actual fracture surface of the bulk material. The surface is rough but does not

Figure 2.17. SEM of a freeze fractured surface of as bulk coagulated 70/30 dope showing the large voids.

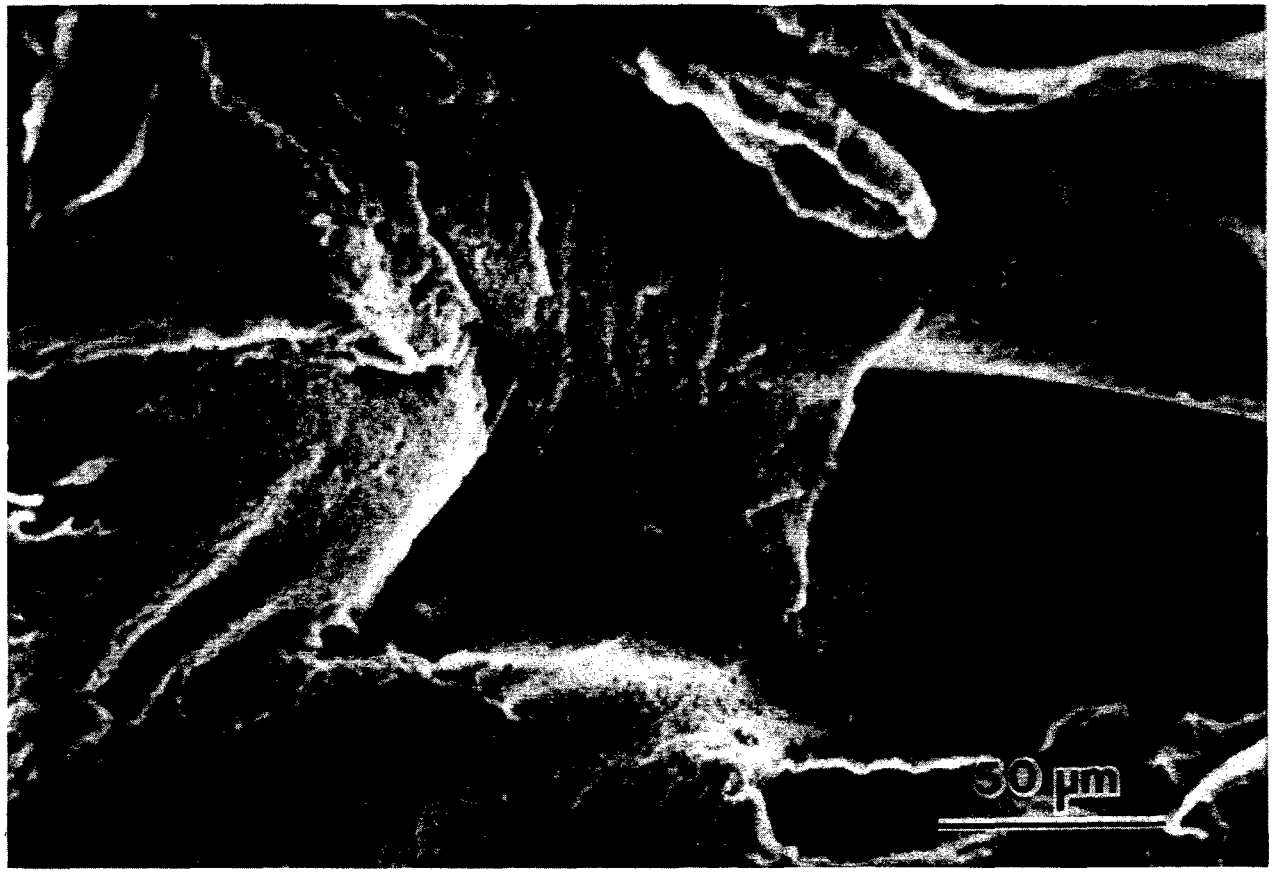


Figure 2.18. SEM showing the morphology of a freeze fractured surface of the coagulated dope.

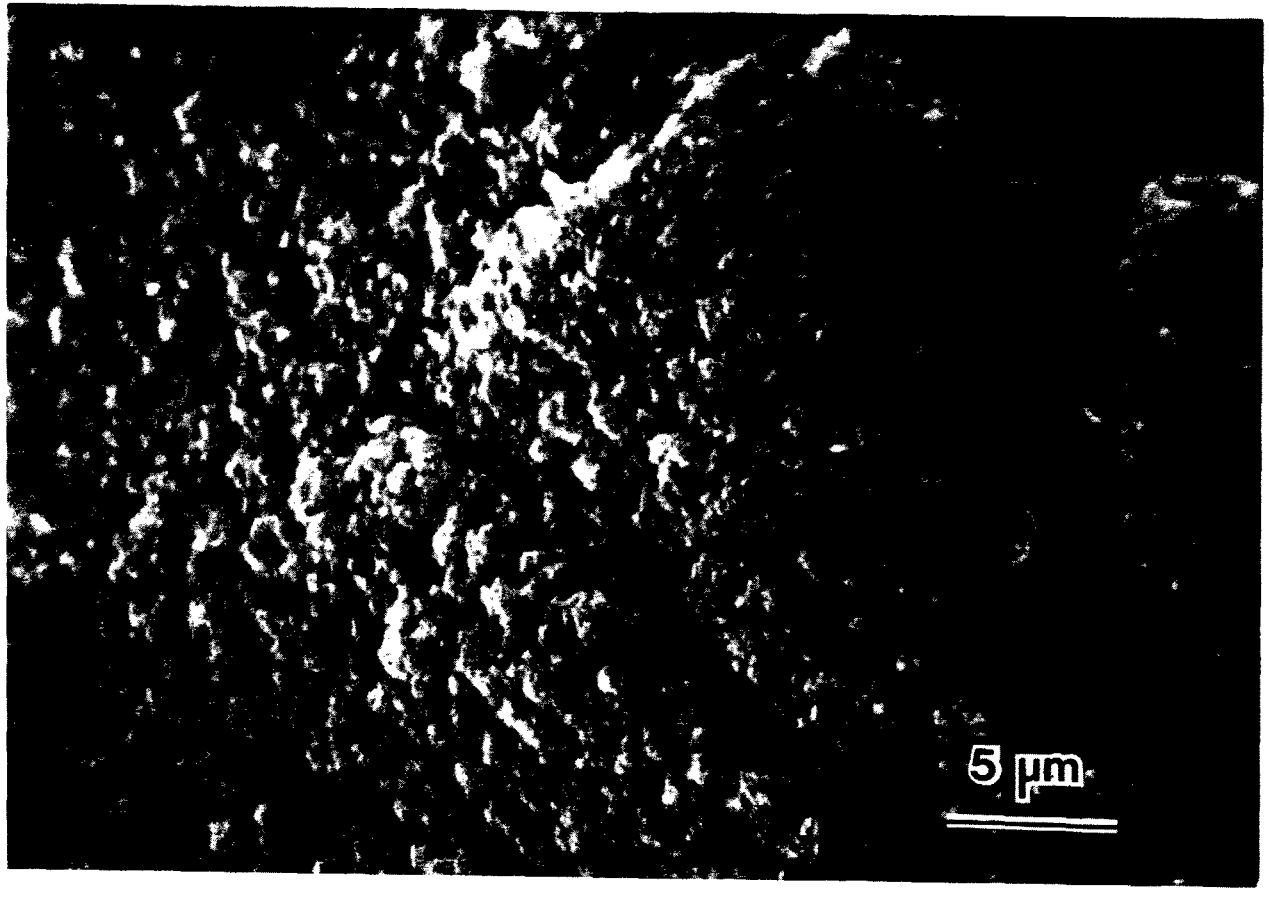


Figure 2.19. Higher magnification micrograph of a selected area of Figure 2.18.

show the phase separated domains as previously observed in a cast PBT/ABPBI film. However, the void surface shows contrasting morphology with phase separated domains. Basically, two types of domains can be found on the void surface. Figure 2.20 shows the surface of a large void with spherical domains. Higher magnification of selected areas (Figure 2.21) shows that these spherical domains vary in size from 1 to 10 μm in diameter and have rough surfaces. Some of the domain surfaces showed smaller ~0.1 μm overgrowth giving a "cauliflower-like" morphology. Figure 2.22 shows a higher magnification SEM micrograph of one of these domains rich in overgrowths. Micro X-ray analysis on these domains shows the presence of S. Since the atoms have lower atomic number, such as C, N could not be detected by X-ray microanalysis, and the rough contour of the domains makes back-scattering imaging difficult. The presence of S can only be an indication of the presence of PBT in these domains and is not conclusive that it is PBT rich.

Another type of the phase separated domains observed on the void surfaces is clusters of spherical to oblong shaped smooth domains 3 to 5 μm size. Such domains are aggregated together such that they impinge on each other. In areas where the domains are removed, indented marks on the surface can be seen in Figure 2.23. This type of morphology is more akin, though not exactly, to the football morphology previously observed.

The probable reason that such domains are formed is during the coagulation process, residual MSA are retained within the voids, partially dissolving the surface such that it is above C_{crit}, resulting in the formation of phase separated domains. The longer the acid remains in the void, the more time it takes for phase separation and the growth of domains to occur. The phase separated domain surface could act as site for further growth of smaller domains, resulting in the cauliflower-like morphology.

Figure 2.20. SEM of a void surface.

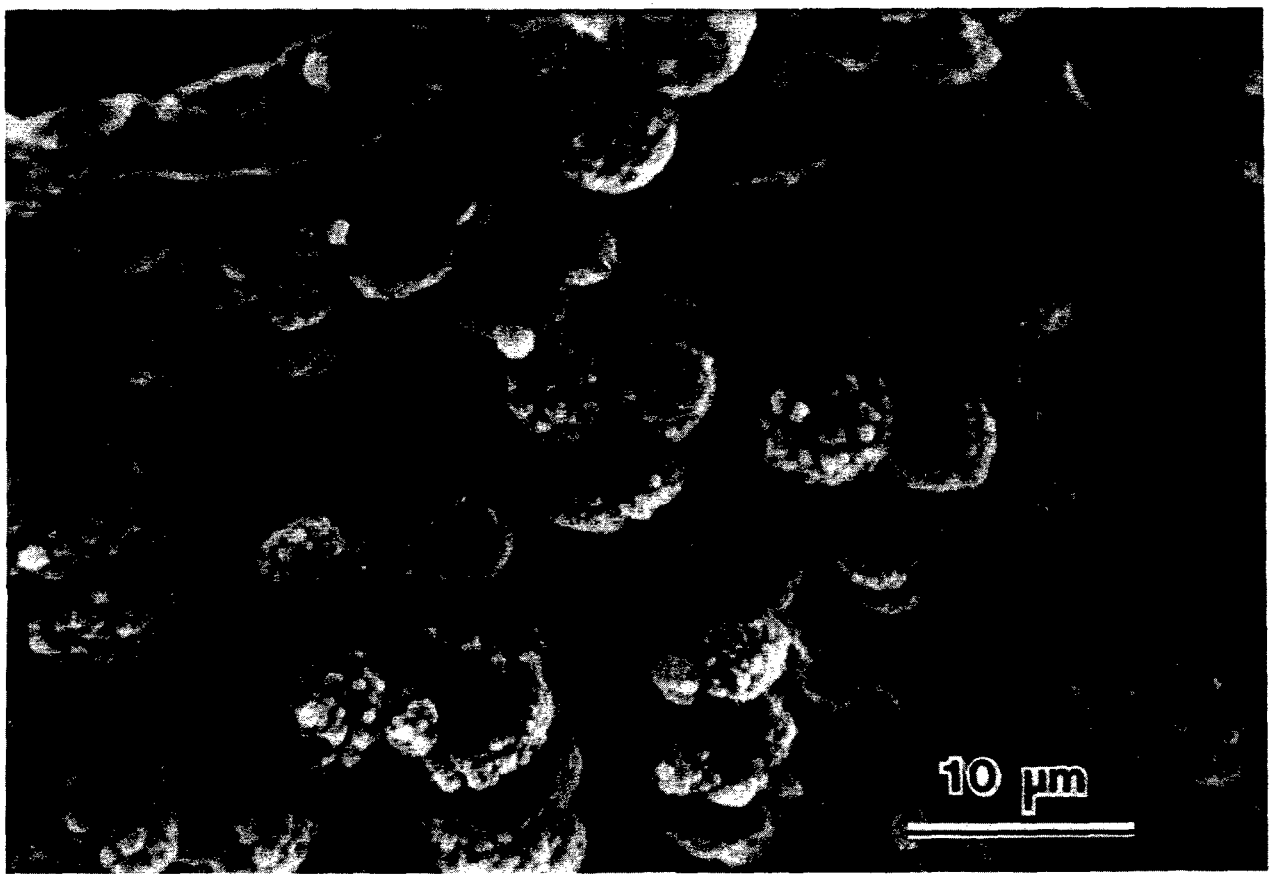


Figure 2.21. Higher magnification micrograph of a selected area of the void surface showing the "cauliflower-like" morphology of phase separated domains.

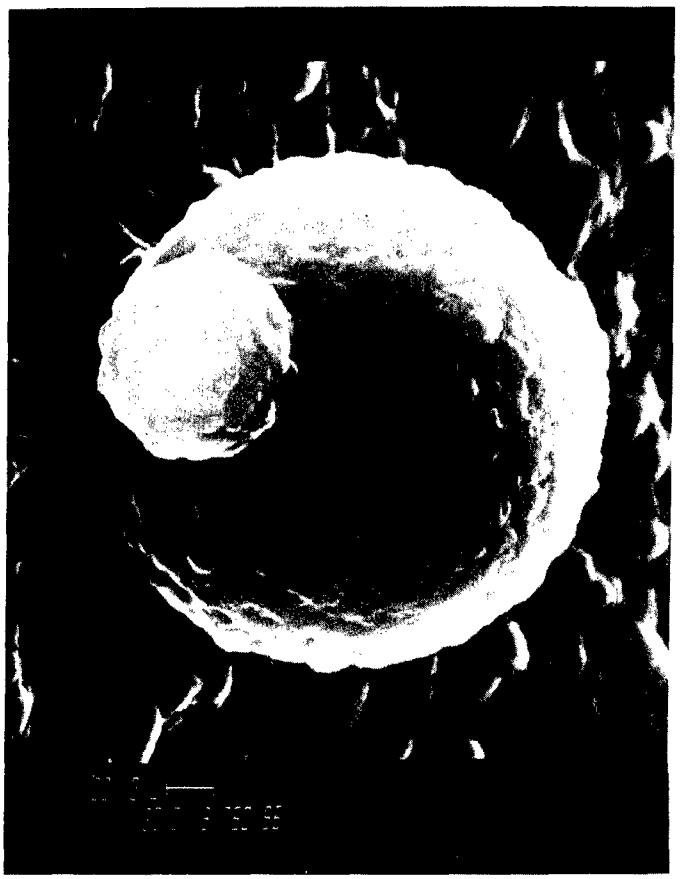


Figure 2.22. Micrograph of an individual domain showing the overgrowths.

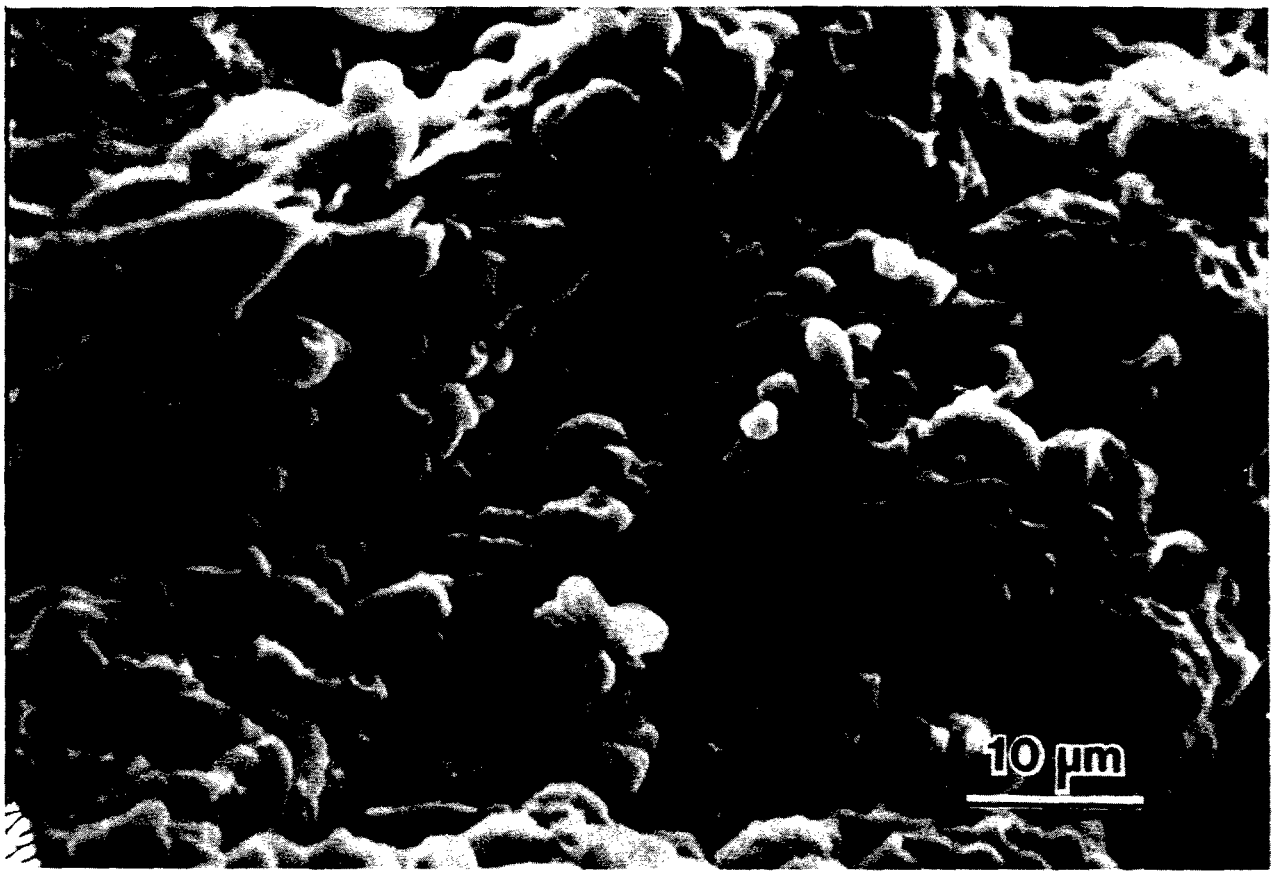


Figure 2.23. Micrograph of the void surface showing the smooth, oblong-shaped domains.

CONCLUSION

Diffusion study shows that coagulation of PBT/Nylon 66/MSA dope follows a power law relationship with respect to dope thickness and coagulation time. The power law indices were found to vary from 0.4 to 0.46 in close agreement to that predicted by a Fickian diffusion. Thus coagulation of thick molecular composite is a slow process governed by diffusion. When the dopes were coagulated without any restraint, there was a drastic change in dimensions with an overall decrease in volume, estimated to be about 50 to 60% and accompanied by the formation of large voids. The void surfaces showed phase separated domains 1-10 μm size; however, these were not observed in the bulk fracture surface. These voids could not be eliminated on subsequent consolidation under pressure and temperature. The presence of voids generates defects and is known to affect the tensile strength tremendously. From the above studies, it is concluded that for direct coagulation a process must be developed to eliminate void formation besides avoiding phase separation.

SECTION 3
BULK COAGULATION OF PBT/NYLON 66 MOLECULAR COMPOSITES

INTRODUCTION

In the coagulation study, we observed that when a PBT/Nylon 66/MSA dope was coagulated without any physical restraint imposed on it, large voids were formed. The void surfaces showed the development of phase separated domains of 1 to 10 μm size. Further consolidation under pressure and elevated temperature could not completely eliminate the voids. As much as 10% void content is still left behind in the consolidated samples. The development of voids during coagulation is undesirable for two reasons. First, the development of phase separated domains on the void surfaces is one to be avoided in the context of obtaining a true molecular composite. The voids also act as defects in affecting the strength of the molecular composite. Thus the effort was directed to scout ways of eliminating macroscopic void formation during the bulk coagulation process.

There are several possible ways of overcoming void formation since it is a result of catastrophic instability process caused by fast coagulation. Changing to a lower power coagulant such as a mixture of water and MSA, or long chain aliphatic alcohols were reported to reduce coagulation rate and suppress void formation in PBT [11]. Lowering the coagulation bath temperature [14] also produced the same effect. An alternate approach which was reported to be successful in eliminating void formation during the coagulation of polyvinyl alcohol in fiber spinning [24] is to gel the solution through the use of boric acid to provide complex formation between boron and the hydroxyl groups.

The present studies explore other possible ways by (1) coagulating under pressure in an autoclave with steam as the coagulant and (2) coagulating in a specially designed mold equipped with a plunger with constant pressure.

STEAM COAGULATION

About 1 cm thick 70/30 PBT/Nylon 66 dope contained in a 3-inch diameter glass jar was put in a small, portable steam autoclave which is capable of producing steam with pressure up to 20 psig and equipped with a safety relief valve. Dopes were coagulated with saturated steam at a controlled pressure ranging from 5 to 15 psig at a temperature of 95 to 105°C. Time, temperature and pressure developed were recorded. At 100°C, 70 minutes is sufficient to coagulate the dope. Figure 3.1 shows a piece of the molecular composite coagulated by this method. Shrinkage occurs laterally. The top surface was exposed to steam and crumbled into a rough, irregular surface. However, the overall thickness decreased and did not bulge out in the center as in the case of bulk coagulation with water, compared to Figure 2.11.

The cross section of a molecular composite so coagulated is shown in Figure 3.2. It appears homogeneously coagulated and free of macroscopic voids. This study shows that even with a modest pressure of 15 psig, void formation can be suppressed such that the overall thickness decreases instead of bulging out as in the direct coagulation with water.

Besides pressure, there are other possible reasons that voids are suppressed. Even though the coagulation temperature is raised to ~100°C, saturated steam at this temperature is only 0.037 lb/ft^3. Compared to the density of water at 60 lb/ft^3, the flux of moisture for coagulation is drastically reduced. Although the rate is accelerated by the higher coagulation temperature, the overall rate in this case could be much less than coagulation using water alone at room temperature.

Another observation is that during coagulation, MSA is exuded out of the dope. Since the dope was contained in a glass jar, MSA remained on the coagulated dope surface giving a mixture of MSA and steam and thus has lower coagulation power. Both the reduced rate and lower coagulation power could contribute in suppressing void formation during coagulation.

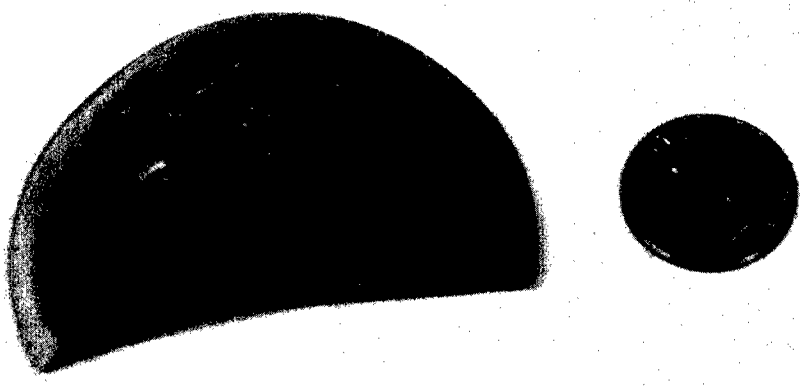


Figure 3.1. Crumbled surface of a steam coagulated dope.

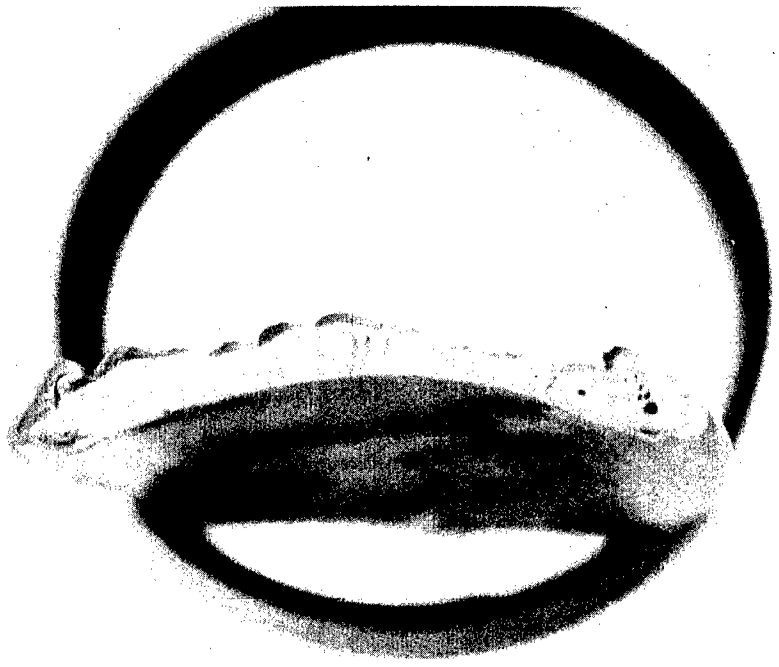


Figure 3.2. Cross section of a steam coagulated dope.

Even though large voids can be eliminated in steam coagulation, the disadvantage of trapping the exuded MSA and the uncontrolled irregular surface formed preclude it from further scouting work at this stage in favor of coagulation using a specially designed mold to be discussed below. However, with suitable modifications in the process, the above disadvantages could be overcome to make steam coagulation as a possible process.

COAGULATION IN A MOLD

An alternate approach in this study is to apply pressure mechanically to the dope during coagulation. This is achieved through the use of a specially designed coagulation mold. About 4 cm thick 55/45 PBT/Nylon 66 dope is put in a stainless steel mold of 1 3/4-inch-square and 3-inch-tall mold as shown in Figure 3.3, and evacuated under vacuum in a dessicator for 48 hours to remove trapped air in the dope. A plunger is inserted on top of the dope and a constant load is applied. The whole setup is put in a trough of running distilled water. Diffusion of the coagulant into the dope is allowed to proceed from the bottom of the mold through a 1/16-inch-thick porous stainless steel plate with 5 μm pore size. In this case, diffusion of coagulant is along one direction only. As shrinkage occurs during coagulation, the plunger moves down under the applied load to contain the volume changes. During the coagulation, it is essential that the movement of the plunger is not impeded by applying sufficient load. In this way, a thick piece of molecular composite can be coagulated without macroscopic void formation.

The time required to coagulate the dope in the mold is estimated from the diffusion study using the power law relationship between x and t. Such a relationship, though established from short time coagulation study, predicted reasonably well with the time required to coagulate thick specimen. For example, a 4-cm-thick 55/45 PBT/Nylon 66 dope of 2.0 wt. % concentration was estimated to take 147 hours to fully coagulate. When coagulation

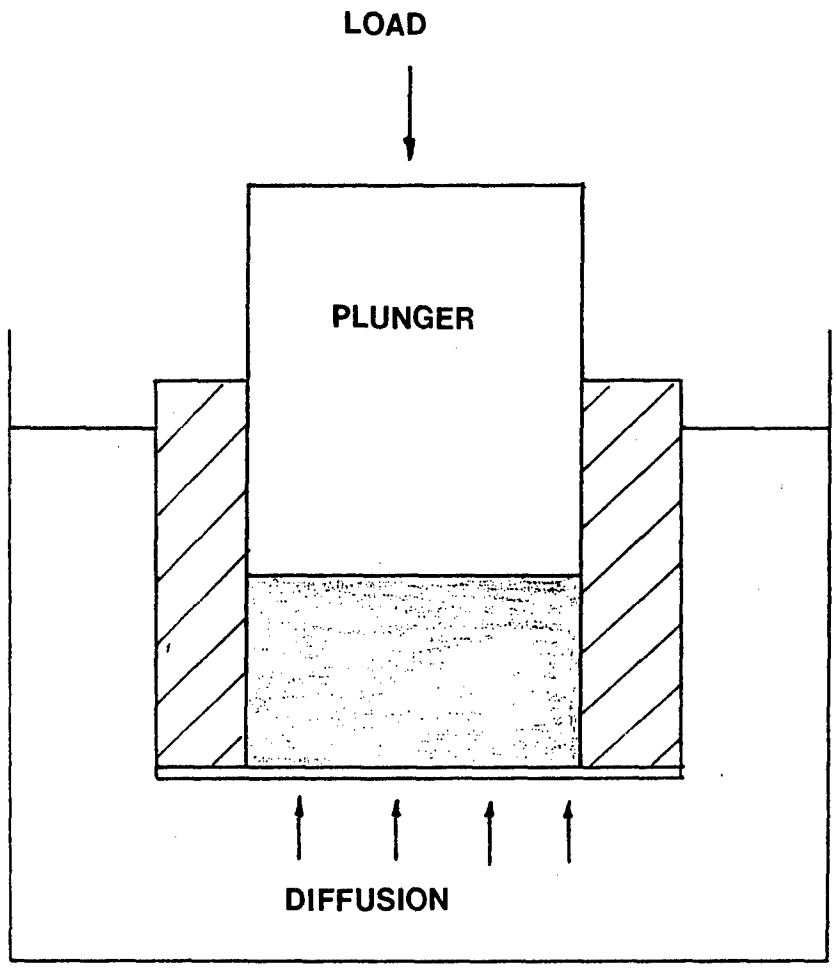


Figure 3.3. Schematic of the mold and plunger used in bulk coagulation.

was stopped after 140 hours, less than 1 mm thick of the dope at the plunger side was not coagulated.

Figure 3.4 shows a dope coagulated by this process. A square piece of molecular composite with uniform thickness throughout the cross section is obtained. After coagulation, the volume was found to decrease by ~50-60%, comparable to what was observed in the coagulation study described in Section 2. Thus the coagulated dope still consists largely of MSA and water. On removing the coagulated dope from the mold, the relief of constraint caused the dope to shrink laterally by ~10%.

From the studies, we found that low pressure is sufficient to suppress macroscopic void formation as long as it is high enough to push the plunger down as the volume of the dope is decreased during coagulation. Figure 3.5 shows the cross section of a dope coagulated under a constant pressure of 5 psi. Large voids are still found near the edges and progressively become smaller towards the center. The number of voids are drastically reduced compared to direct coagulation without pressure application. When the pressure was increased to 9 psi, a relatively void-free specimen was obtained (Figure 3.6), the cross section appeared to be homogenous and macroscopic voids are not observed under optical microscope up to 400X magnification. Although the pressure increase is small, the key is that the downward movement of the plunger is not impeded.

After coagulation, a semi-rigid gel-like mass of molecular composite is obtained. It is washed with running distilled water for at least 7 days to remove the remaining acid. When a 55/45 PBT/Nylon 66 specimen prepared in this way is dried in air, its fracture surface is examined with SEM. Microvoids up to 10 μm are present (Figure 3.7). It is difficult to conclude that such microvoids are initially present in the coagulated dope since the drying process reduces the mass of the solvent-rich gel-like coagulated dope without the corresponding volume decrease and thus must create voids during the drying process. Close examination of the voids did not show the formation of domains compared

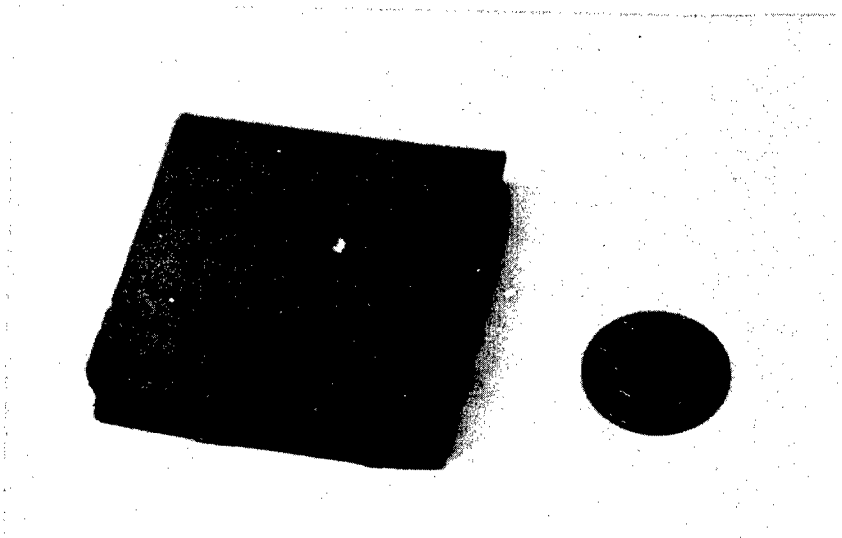


Figure 3.4. A piece of 55/45 PBT/Nylon 66 dope after coagulation in the mold.

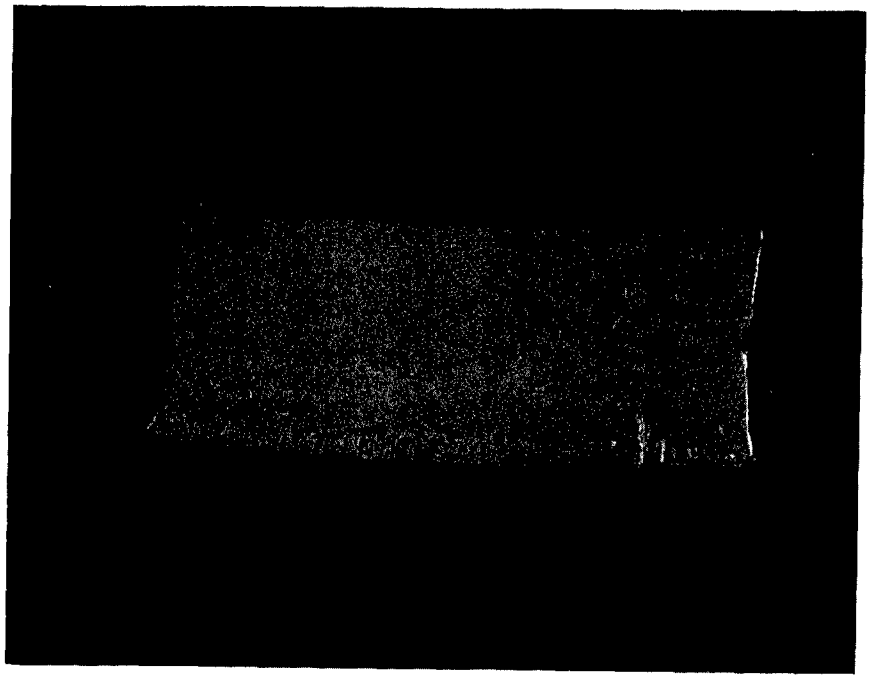


Figure 3.5. Cross section of a dope coagulated in the mold at 5 psi pressure, containing voids.

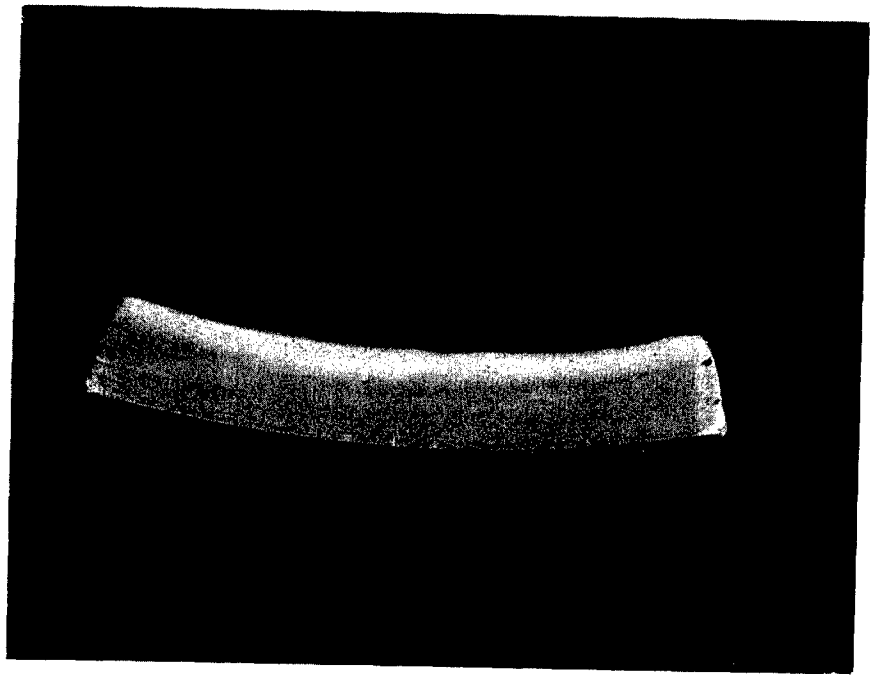


Figure 3.6. Cross section of a relatively void-free dope coagulated in the mold at 9 psi.

Figure 3.7. SEM of a freeze fracture surface of dope coagulated in the mold and dried in air, showing the presence of microvoids.

to those found previously on the surface of large voids (Figure 2.17). Even in thin film extrusion using a coat hanger die, spherical domains are formed on the surface of 30 μm size void. Thus the absence of such domains in the microvoids could indicate that either they are formed only during the drying of the coagulated dope, or if microvoids are present during coagulation, their sizes are too small for the formation of domains on their surfaces. Higher magnification with SEM did not show gross phase separation of domains up to 1,000 A resolution.

After coagulation and washing, the molecular composite is still composed largely of water which had to be removed through further consolidation process to reduce it to its final thickness. This is done by pressing the coagulated dope in a mold at an elevated temperature.

We found that when consolidation is done by allowing the sample to flow lengthwise under pressure up to 25% elongation, cracks are formed perpendicular to the flow direction. Therefore, the specimen has to be consolidated in a close mold without lateral flow but only thickness reduction.

The coagulated dope was cut into a rectangular piece of 1(1/2) inches by 1/2 inch to fit the mold and consolidated using a Tetrahedron Smart Press which is programmed to increase or hold the pressure and temperature at a specified rate. The consolidation cycle is shown in Figure 3.8. The sample was preheated in the press at 85°C for 1/2 hour and pressure was applied from atmospheric to 4,000 psi at a rate of 28 psi/min and held for 1 hour. During this stage, water is squeezed out. Further drying was continued at this pressure by increasing the temperature to 180°C and allowed to dry overnight for at least 16 hours. After which the pressure was reduced to 500 psi and temperature raised to 275°C to melt Nylon 66. The pressure was reduced to avoid squeezing out the nylon and the pressure effect on raising its melting point. Pressure was then increased to 4,000 psi for 1-1/2 hours before it was finally cooled down.

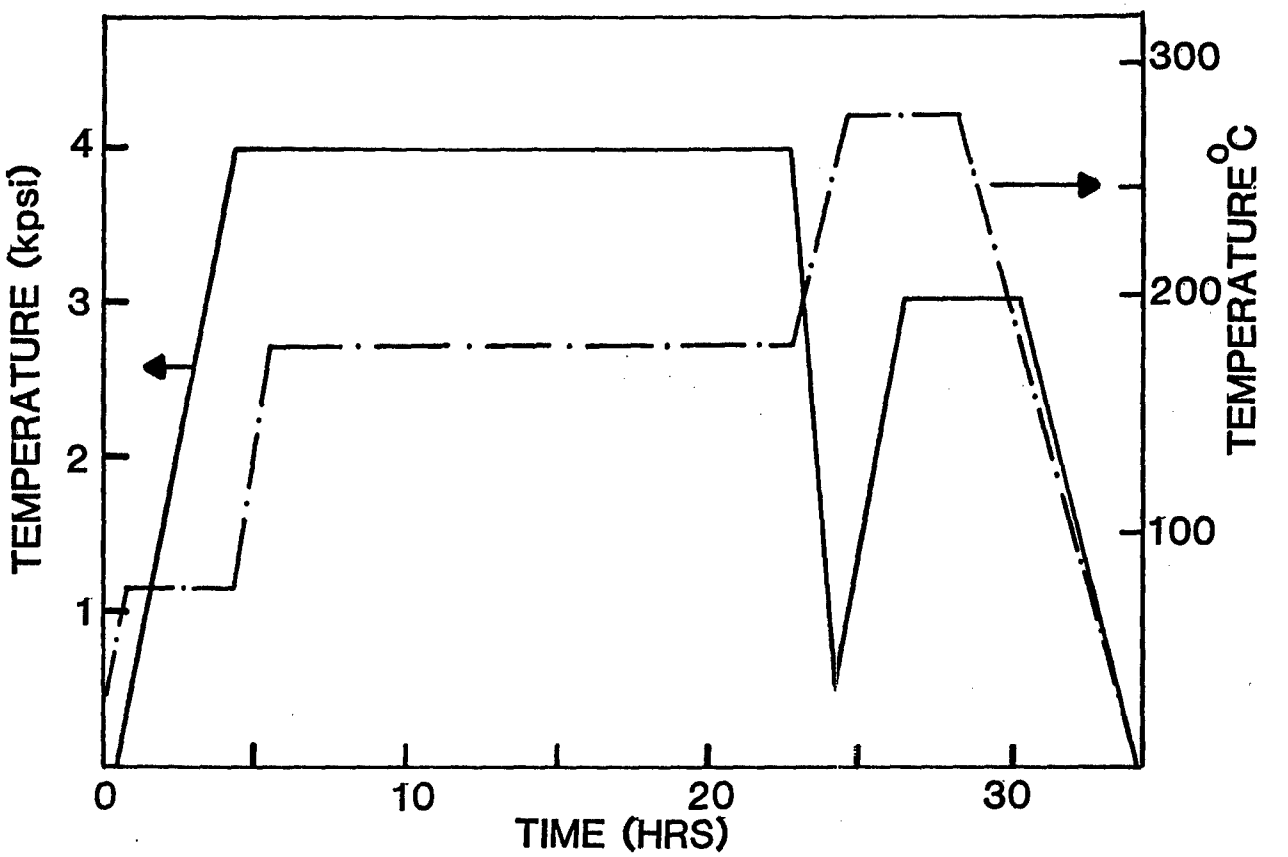


Figure 3.8. Temperature and pressure cycle used in the consolidation of coagulated dope.

55/45 PBT/Nylon 66 molecular composite processed this way was tested for its mechanical property. The specimens were mounted with tabs at the end for gripping, a strain gauge was mounted on the flat surface of the sample and tested with a MTS tensile tester at a strain rate of 0.01 $min.^{-1}$ The average moduli is 2.5 mpsi and a tensile strength of 11 ksi with elongation at break of 0.6%. The tensile strength and elongation at break are of lower estimates since the samples broke near the grip. However, the modulus obtained is much lower than the 3.45 mpsi reported for a 50/50 PBT/Nylon 66 consolidated by the lamination of wet filaments process [25].

The morphology of the consolidated molecular composite was examined with a SEM from freeze fracture surface (Figure 3.9). Two features can be seen from the micrograph. It shows the presence of ~0.1 μm size domains not previously observed in the air dried specimen before consolidation in a hot press. These are likely to be the phase separated domains since consolidation took place at temperature above Nylon 66 melting point, in which the polymer chains have sufficient mobility for phase separation. Subsequent studies by SEM and time-resolved small-angle light scattering on the effect of consolidation temperature on phase behavior of molecular composite showed that at temperature above the onset of differential scanning calorimeter endotherm, phase separation begins rapidly with the domain sizes growing both as a function of temperature and time.

The second feature is the layer-like structure. This occurs as a result of squeezing down the thickness direction by the application of pressure. Such phenomena has also been found in the squeezing flow deformation of polypropylene [26]. The collapse of the volume accompanied by the loss of water through squeezing caused cracks to initiate and propagate in the direction perpendicular to the squeezing direction and the formation of layer-like structure.

Figure 3.9. SEM of a freeze fracture surface of the dope after consolidation under pressure and temperature showing the layer-like structure.

SCALE-UP MOLD AND FURTHER DEVELOPMENT

From the above studies, a process was identified to coagulate molecular composite dope directly into bulk specimen without macroscopic void formation using a coagulation mold to obtain larger and thicker specimens for further mechanical property investigations and to control the process better. A scale-up mold is designed as shown in Figure 3.10. The mold is machined from Hestalloy B2 steel for corrosion resistance from MSA and has an internal dimension of 3 1/2-inch square such that six dumbbell test specimens can be obtained from a single coagulated molecular composite. The height of the mold is 8 inches tall giving the final consolidated thickness of up to 0.1 inch thick. A Teflon plunger which is slightly tapered such that the upper dimension is 2 mil larger than the mold is force fitted into the mold to prevent dope leakage through the plunger when pressure is applied. The plunger carries a Dynisco pressure transducer with a range of 0 to 100 psi and its surface is flush in contact with the dope. A bleeder is provided on the plunger to allow air to escape when the plunger is force fitted into the mold. The plunger is connected to the drive shaft of a motor from the top and is controlled to move down under a controlled constant pressure. Such control will allow the pressure to be maintained so that the plunger is always touching the dope to accommodate the volume changes during coagulation. A thicker 1/8-inch stainless steel porous plate is used for coagulant to diffuse into the dope and gasket is used to prevent leakage of dope. The whole assembly is then immersed in a trough of running distilled water during coagulation.

As the coagulation of bulk dope is a slow process, the following variations can be made to reduce the coagulation time:

(1) hot water coagulation. Since coagulation is diffusion controlled, the diffusivity of the coagulant can be increased by increasing the temperature.

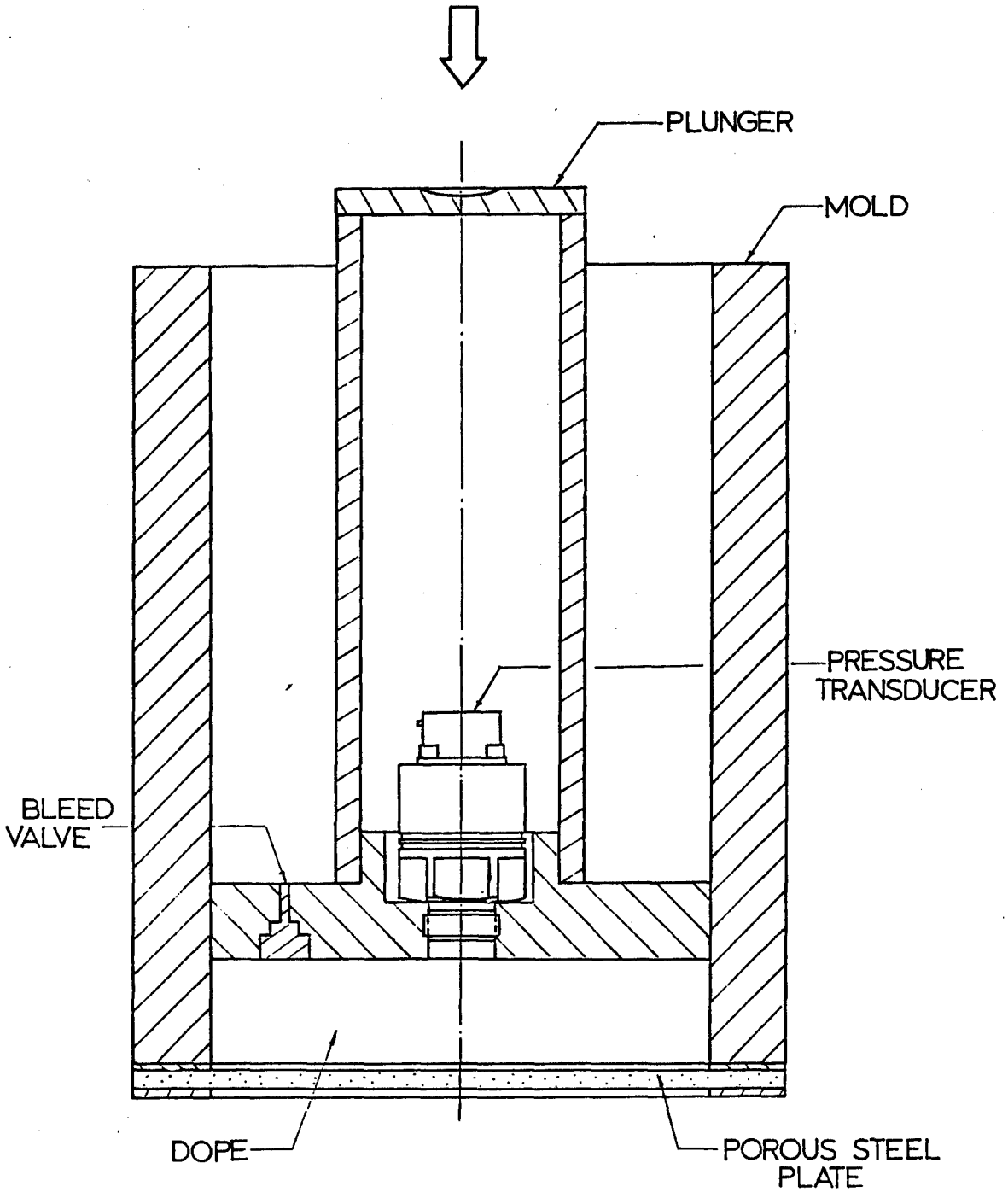


Figure 3.10. Schematic of the scale-up mold.

(2) the use of alkali solution for coagulation such that diffusion of the coagulant is accompanied by a neutralization reaction with MSA.

(3) The mold design can be modified such that the plunger is made of porous stainless steel to allow diffusion to occur from both ends of the mold. This is equivalent to reducing the thickness of dope by half and therefore the coagulation time is correspondingly reduced by about 5 times according to the power law relationship from coagulation studies.

The above modifications form part of the future developmental research in the direct coagulation approach.

SECTION 4
OTHER NON-MELT CONSOLIDATION STUDIES

This section describes the studies of other approaches in the non-melt consolidation of molecular composite. The ultimate goal of such studies is to obtain thick molecular composite because they are either impractical or difficult. They were not selected for development in favor of the direct coagulation using a mold as described in the previous section. However, the studies are recorded for reference if future development is needed.

MULTI-FILM COAGULATION

The objective of this approach is to build up film thickness by layering the dope over previously coagulated specimen one at a time.

A 70/30 PBT/Nylon 66 dope (2.0 wt. % concentration) was spread on glass plate by spatula into thin film. An alternate way of spreading was to use a spreading doctor blade which has an adjustable knife edge to control the dope thickness for spreading. However, we found that due to the high viscosity of the dope, it did not flow easily and was therefore not practical. Spreading dope using a spatula is easier.

The spread dope, about 3 to 5 μm thick, was coagulated in distilled water for 5 minutes. The coagulated dope was yellow and transparent. A second layer of dope was then spread on top of the coagulated film. We found that with the wet surface, the dope could not be spread easily and there is no adhesion between layers. Thus the first layer of film has to be dried before a second layer of dope can be applied.

Drying was carried out by blowing with a hot air gun. Lateral shrinkage occurs during drying, however, and the film still adheres to the glass plate. On applying a second layer of dope, the color of the dried first layer film was observed to change from orange to light yellow. This was due to MSA from the

newly applied dope either partially dissolving the dried film or protonating the PBT to give the yellow color. By carrying out this process of drying and spreading of fresh dope, the film thickness can be built up. However, there are problems associated with such a process:

(1) Due to the lateral shrinkage of the film during drying, the surface of the film became wrinkled, making the application of dope difficult.

(2) As the thickness is built, the shrinkage finally caused the film to separate from the glass surface.

Due to the above problems, less than 10 layers can be applied in this way. A solution to overcome this was tried: the dope was spread on the outer surface of a glass cylinder with a diameter of 1.5 inches. When the coagulated film shrank on drying, the shrinkage caused the film to wrap tightly around the cylinder. Then new dope was applied to the outer surface. Such shrinkage will ultimately produced hoop stress on the coagulated film.

FINE PARTICLE COATING METHOD

A 0.5 wt. % solution of 55/45 PBT/Nylon 66 in MSA was prepared. This dilute solution can be sprayed into fine mist of 50 to 200 μm size with the use of an atomizer. The objective is that such fine mist of dope can be coagulated very rapidly when it comes in contact with a coagulant to "freeze" the structure of the molecular composite. The coagulated particles can be sintered into thicker specimen. The fine mist could also be sprayed onto a hot surface such that the solvent is evaporated rapidly leaving a molecular composite film built up of fine particles. These two variations were tried.

Sintering of Molecular Composite Particles

The 0.5 wt. % solution was sprayed with an atomizer into fine droplets of about 100 to 300 μm size with a compressed air can onto a jar of distilled water with stirring. The sprayed

droplets coagulated and floated on top of the water. Spraying process was very slow. Only a small quantity of particles was collected by filtration on a glass frit, about 1.5 cm in diameter. The filtered particles were washed with water, followed by ethanol and dried in the frit by pulling under vacuum. The particles formed a mat which was removed from the frit and was further pressed between layers of filter papers under pressure of 5,000 psi in a Carver hand press. On removing the pressure, it was found that the mat cracked under such pressure.

Casting of Molecular Composite Droplets

The same dilute solution was sprayed with an atomizer directly onto a glass plate which was preheated to 200°C on a hot plate in a fume hood. Even though MSA has a boiling point of 167°C at 10 mm Hg, the large surface area of the droplets caused rapid evaporation of MSA at the casting temperature, with fumes of MSA evaporated. In this way, the glass plate was coated with transparent cast molecular composite film made up of fine particles (Figure 4.1). The particle size varies from 50 to 300 μm and appeared to be featureless under optical microscope (Figure 4.2) showing the homogeneity of the particles except the edges. Figure 4.3 shows the same film under cross-polars, the particles extinct except at the edges which are birefringent. The film formed was very thin and adhered to the glass slide tenaciously, and was difficult to peel off.

The above two methods show that it is possible to obtain molecular composite film through the aggregation of fine particles, but the process of casting is a tedious one to build up film thickness. However, the process of sintering the particles does have potential since it is an important industrial process in metal and ceramic forming, and has been used to process Teflon [27]. Industrial atomizers [28] can be used to make the particulate molecular composite of controlled size more rapidly. Subsequent compaction of the particles and the eventual molecular diffusion between particle boundaries should result in a coherent piece of molecular composite.

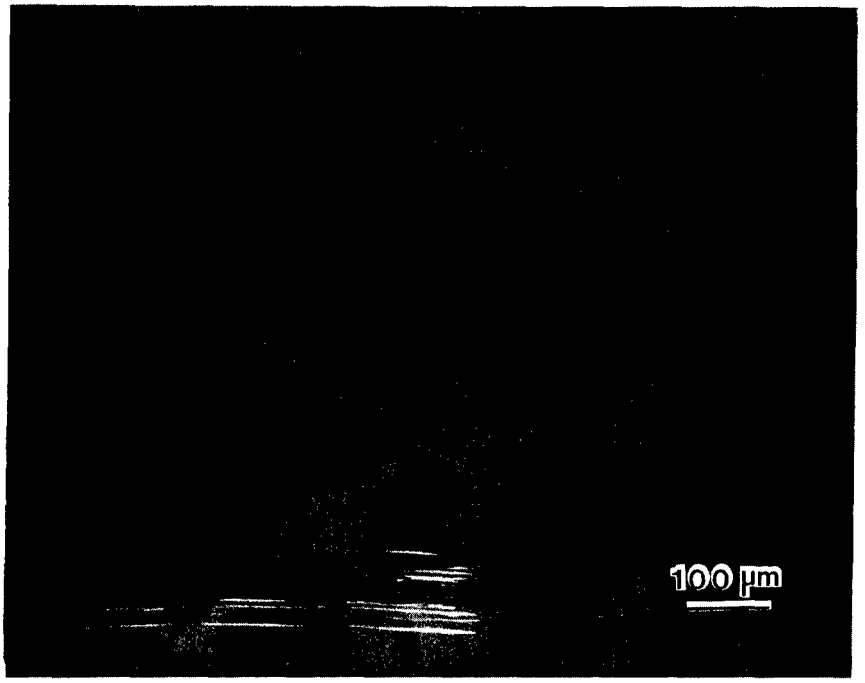


Figure 4.1. Optical micrograph of the particle deposits after spraying on a hot plate.

Figure 4.2. Higher magnification of the above particle showing the homogeneity.

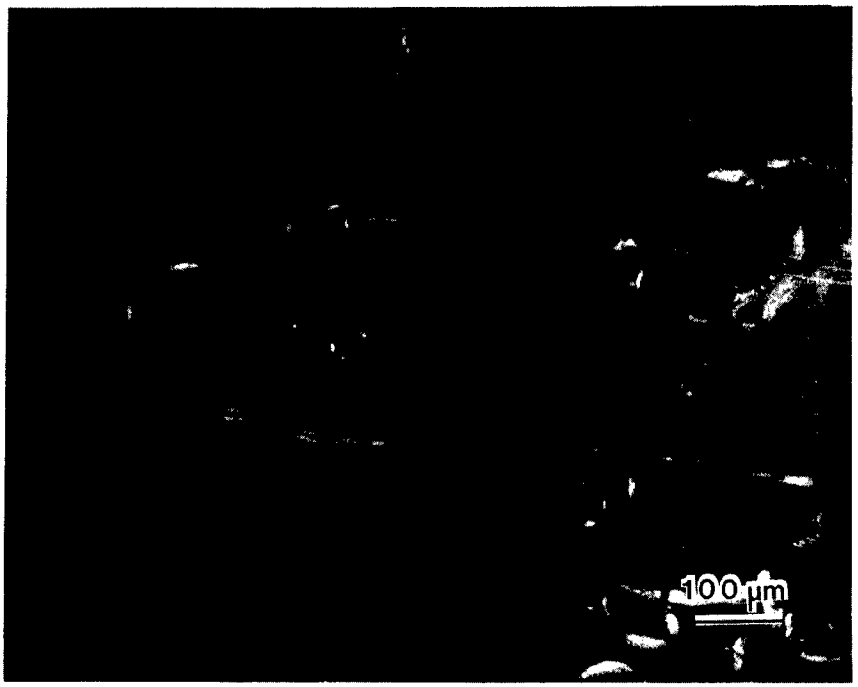


Figure 4.3. Figure 4.1 under cross-polars.

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APPENDIX

Coagulation of PBT from PPA Dope

The PBT/PPA dope was cut into small pieces about 1/2 to 3/4 inch size and was boiled in distilled water at about 70°C for about 1 week. The water was changed every day and boiling continued until pH was neutral. The washed PBT was then dried in a vacuum oven at 100°C for 36 hours. The dried PBT pieces were ground into small flakes with a grinder and further dried in the oven. The final PBT was then checked for phosphorous content by elemental analysis for traces of residual pf PPA. If P content was 0.5%, then the flakes were further boiled and dried.

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